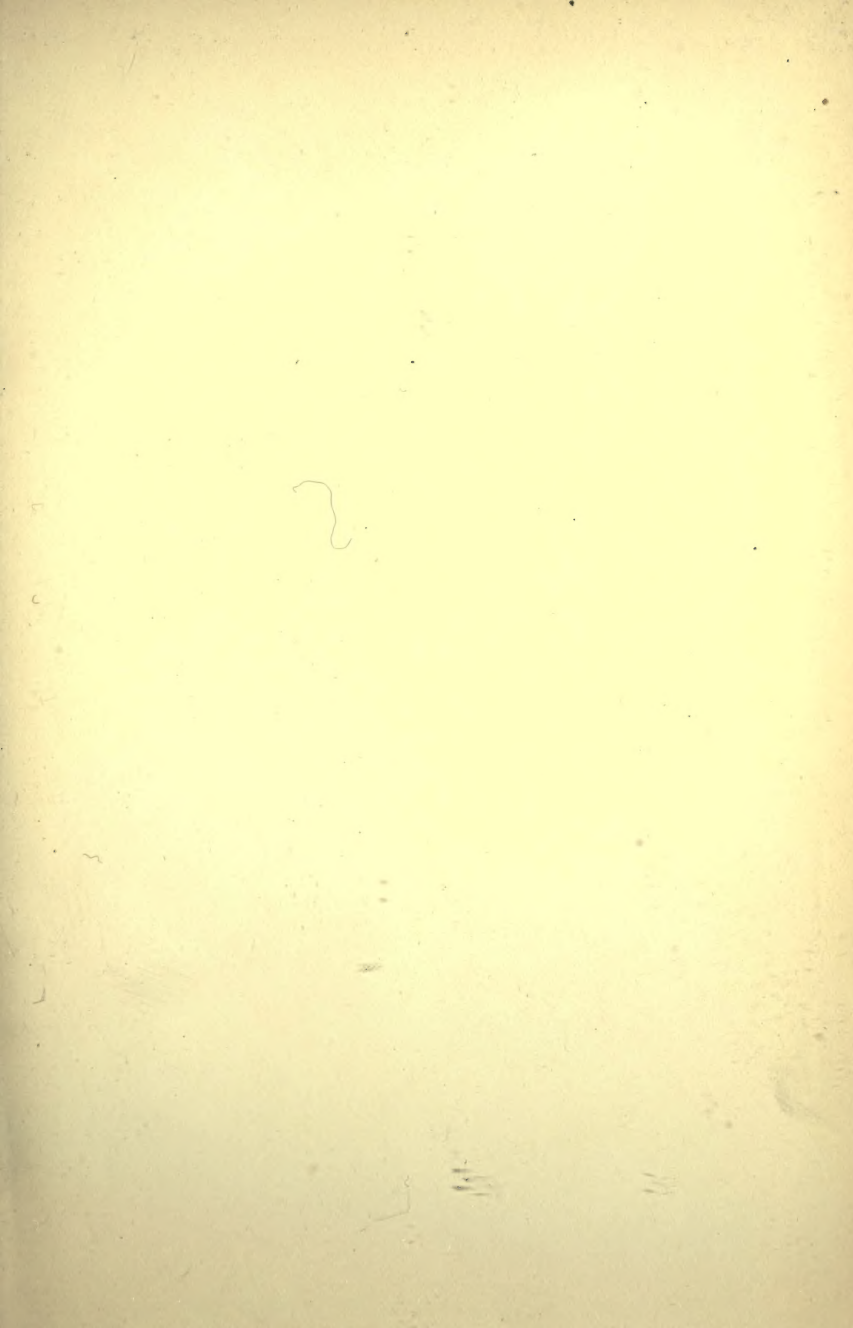




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*Laboratory Exercises in
Physical Chemistry*

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Laboratory Exercises in Physical Chemistry

John Norman BY
J. N. PRING, D.Sc.

Lecturer and Demonstrator in Electro-Chemistry

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PREFACE.

THE laboratory exercises described in this text book are designed to meet the requirements of students who wish to follow a laboratory course dealing with some of the applications of physical chemistry. The experimental work here described is based on the exercises introduced by Dr. R. S. Hutton, in 1900, as a supplement to the course in practical physics which form part of the curriculum of the students in the Honours School of Chemistry in the University of Manchester, in their first and second years' studies.

It has been endeavoured, in this collection of exercises dealing with certain branches of chemical physics, to present to chemical students a publication which will for their purpose supplement the text books of Schuster and Lees, on "An Intermediate Course in Practical Physics" (Macmillan & Co.), and "Advanced Exercises in Practical Physics" (Cambridge University Press), and it is expected that students following this work will have already taken one or both of the above courses in pure physics.

The field in the borderland between physics and chemistry has grown to dimensions which are now very large and is still rapidly increasing. In this text book it has consequently only been attempted to deal with a few phases of this subject, and

these lie mainly in the domain of electro-chemistry and the closely allied subject of high temperature chemistry. The close association of this latter with electro-chemistry is due to the fact that electrical methods of producing and of measuring high temperatures are now very widely used in chemical research work. Not only for producing temperatures above about 1800° , where no other practical method of obtaining definite high temperatures is available, but in the region of comparatively low temperatures, such as between 1000° and 1500° , electrical heating, on account of the facility with which it can be applied and controlled, has largely supplanted the use of gas and fuel furnaces in laboratory work.

This book also deals with part of the ground covered by students who specialise in electro-chemistry in their third year's studies for the Honours degree; but the remaining part of this course on applied electro-chemistry, which relates to electric furnace work has been omitted, as the ground is covered by the publication of Mr. R. E. Slade on "Laboratory Electric Furnaces." *

The scope of this book has been limited almost entirely to the experimental details in laboratory manipulations, while the theoretical side has been only very briefly indicated. The introduction of thermo-dynamics has only been made to point out the important bearing that this has when applied to such measurements as those of electrode poten-

* Constable, London.

tials, decomposition voltages, and polarisation, the theoretical aspects of which have been fully dealt with in numerous existing publications. For a fuller treatment of the subjects in this book, the student is referred to Ostwald-Luther's "Physico-Chemical Measurements"; Nernst, "Theoretical Chemistry"; Foerster, "Elektrochemie wässriger Lösungen"; Elbs, "Electrolytic Preparations"; Le Chatelier and Wologdine, "High Temperature Measurements"; and publications in the scientific journals, to which reference is given in the text.

I wish to express my indebtedness to Mr. A. Parker for his able assistance in the preparation of the diagrams.

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Laboratory Exercises in
Physical Chemistry



PART I.

PHYSICO-CHEMICAL MEASUREMENTS.

1. MOLECULAR WEIGHT DETERMINATION BY LOWERING OF FREEZING POINT.

RAOULT, who was the first to investigate systematically the lowering of freezing point produced by the solution of different bodies, was led to formulate the important generalisation that equimolecular concentrations of different substances produce, in the same solvent, the same lowering of the freezing point. Thus, if T_0 be the freezing point of a pure solvent and T_1 that of a solution containing g grams of the dissolved substance in 100 grams of the solvent, and M be the molecular weight of the substance dissolved, then $\frac{M(T_0 - T_1)}{g}$ equals the

molecular lowering of the freezing point, which, as Raoult found, is, for one and the same solvent, a constant, *i.e.*, $\frac{M(T_0 - T_1)}{g} = K$.

K can be evaluated by determining the depression produced by substances of known molecular weight. It has moreover been theoretically deduced on thermo-dynamic grounds by Van't Hoff, who found the relation between the lowering of freezing point and the latent heat of fusion of the solvent (*see page 7*).

For the calculation of molecular weights from

observations of the lowering of freezing point, we can make use of the formula $M = K \frac{g}{T_0 - T_1}$, or, if x equals the weight of substance dissolved in y grams of the solvent $M = K \frac{100x}{(T_0 - T_1)y}$.

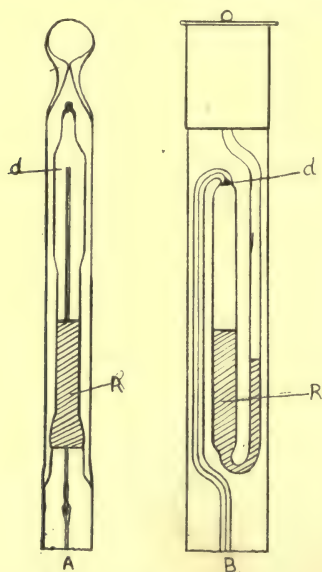


Fig. 1.

The value of K for Water = 18.7

Acetic acid = 38 (M.P. = 16.5°)

Benzene = 50 (M.P. = 5.4°)

Apparatus. The form of apparatus most generally employed is that of Beckmann. The

thermometer is of special construction, having a very open scale and only comprising an interval of about 4° . The top of the thermometer tube terminates in a small reservoir containing mercury (R, Fig. 1), so that the quantity of mercury in the bulb can be regulated, and the scale interval adjusted for different temperatures. The adjustment of the thermometer is made with the help of an ordinary thermometer in the following way:—The two thermometers are immersed in a beaker of water whose temperature is $1-1\frac{1}{2}^{\circ}$ above that of the freezing point of the solvent. The mercury should now fill the whole thread of the thermometer and extend a short way into the reservoir, as shown at *d* (Fig. 1, B). The thermometer is removed from the beaker, and while cooling, connection of the mercury thread with the reservoir is severed by tapping at *d*, while carefully supporting with the hand behind this place. In both types of thermometers, A and B, this action displaces the mercury from *d* to the bottom of the reservoir R. If the reading should lie too low on the scale—leaving insufficient range for the depressions of the freezing point to be observed later—it is necessary to add more mercury from the vessel to that already contained in the bulb. This is done by carefully warming the thermometer until the mercury in the thread is continuous with that in the reservoir. (The latter is brought to the top of the reservoir by a centrifugal motion.) The adjustment is then made as before. (Before commencing an experiment, it is

always advisable to take a measurement of the freezing point of an unweighed sample of the pure solvent.)

Practical. As a good example of these determinations the molecular weight of camphor in glacial acetic acid may be taken. However, on account of the hygroscopic nature of this solvent, precautions must be taken to prevent access of air during the experiment. A small quantity of the glacial acetic acid should be fractionally crystallised two or three times by cooling the liquid until partially solidified and then pouring back the mother liquor into the main bottle. The final solid fraction—about 20—25 cc.—is then quickly transferred to the previously weighed tube, and well stoppered from the air.

The outer jar of the apparatus is filled with some cooling mixture so as to be about 5—10° below the freezing point of the solvent. About 20—25 cc. of the solvent is weighed on a rough balance to within about 2 centigrms. or 0.1%, and placed in the well-corked inner tube C, which has previously been carefully dried. The cork holding the thermometer and stirrer is then inserted and the tube slightly under-cooled by direct immersion in the cooling liquid of the outer vessel for a short time. An under-cooling of about 1° is advisable, but not so that any solvent freezes out. The tube is then dried externally and placed in an air mantle. On vigorous stirring, the solvent should now begin to solidify. The

thermometer will rise for some time and then as a rule slowly fall. The highest temperature indicated is taken as the freezing point and must be noted to $\frac{1}{1000}$ degree. (The thermometer should be tapped during the temperature readings.)

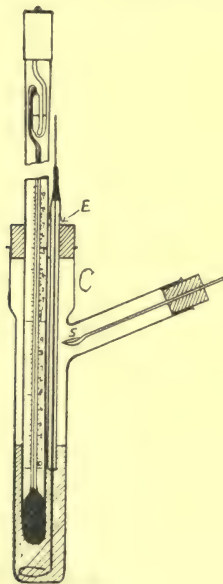


Fig. 2.

The solvent is then re-melted (usually most conveniently done by warming the tube in the hand) and the observations should be repeated twice more.

About 0.2gram. of the substance to be dissolved is, after careful weighing, introduced by the side

tube so that it falls into the solvent without touching the sides of the tube. After complete solution, observations of the freezing point are taken as before and again repeated a third time. These measurements should then be repeated with larger quantities of the substance, say, 0.4 gm. and 0.6 gm.

[NOTE 1.] To obtain any accuracy in these measurements, several precautions have to be carefully observed in order to avoid the main sources of error which arise. If the solvent which is used is hygroscopic, the chief error is that produced by absorption of water from the atmosphere. In this case, the solvent must first be carefully dehydrated, and when in the tube must be well protected from the air. The solute can be introduced into the solvent without removing either of the stoppers by means of a spoon-shaped glass spatula, as shown at S (Fig. 2). To make this spatula, a small bulb is blown on the end of a glass tube, and then one side is drawn in to make half the surface concave, and the bowl then bent up a little.

The solid is kept in this hollow during the freezing point measurement of the pure solvent, and then by turning the spatula round, can be dropped into the liquid. Means should also be adopted to prevent the entrance of air, during stirring, through the space between the stirrer and the channel of the cork E. Another uncertainty in the measurements is caused by the fact that during the reading of the freezing temperature, on account of radiation to the colder surrounding jacket, the solution will always be somewhat undercooled.

Thus, the apparent freezing point t_1 will be lower than the true freezing point t_0 by an amount $\frac{v}{k}$, where v is the rate of cooling by radiation to the enclosure, and k the rate of heating by the freezing of the liquid, so that $t_0 = t_1 + \frac{v}{k}$

or, more correctly, $t_0 = t_1 + \frac{v-v_1}{k}$ where v_1 equals the rate of heating on account of the stirring.

To eliminate this error, v must be made very small, and k very large; v the radiation to the enclosure depends on the difference of temperature between this and the solution, so that the enclosure should be at a temperature not more than a few degrees below that of the freezing point of the solution. k , on the other hand, is made as large as possible by stirring rapidly, and by the presence of a large surface of the frozen solvent. The quantity of this present is determined by the amount of supercooling in the first place. If this is too great, however, another error predominates, viz., that caused by having increased the concentration of the solution through the freezing of the solvent. The magnitude of this effect can, however, be calculated and allowed for.

It is necessary, for these measurements, that the solvent should be made to separate in the form of very small crystals, so as to offer a large surface. For this reason, when working with some solvents, it is very difficult to obtain an accurate freezing point measurement on account of the tendency to the formation of solid in a massive condition. Measurements with organic substances are usually most conveniently made by using acetic acid or benzene as the solvent, though in the former case special precautions must be taken on account of its hygroscopicity.

[NOTE 2.] The value for the molecular lowering of the freezing point K was deduced thermo-dynamically by Van't Hoff, who found the relation between the lowering of freezing point and the latent heat of fusion of the solvent. To make this calculation a cyclic process must be imagined to be carried out as follows :—

We take a dilute solution containing n grm. mols. of dissolved substance in P grams of solvent. We now imagine two heat reservoirs, the first at the temperature T_1 , the freezing point of the solution, and the second at T_0 , the freezing point of the pure solvent. Beginning the cyclic

process with the solution at T_0 , this is placed in the first reservoir and cooled down to T_1 , at which temperature as much of the pure solvent is allowed to freeze out as corresponds to the volume in which 1 gram. mol. of the dissolved substance is contained, i.e., $\frac{P}{n}$ grms. of the solvent. On account of the large volume of the solution, the slight change in concentration during this process can be neglected. The heat given out during the change at this temperature T_1 is equal to $\frac{PL}{n}$, where L is the latent heat of fusion of the solvent. The solution and the solidified solvent are then placed in the second reservoir where their temperature is raised to T_0 . The amount of heat supplied to raise the temperature here will be equivalent to that yielded during the first cooling from T_1 to T_0 . The solid is here allowed to melt, whereby $\frac{PL}{n}$ calories are absorbed. The fused solvent is then allowed to enter the solution through a semi-permeable diaphragm, so as to produce the maximum amount of work osmotically. The work will equal $PV = RT_0 = 2T_0$. The system will now be in its original condition. An amount of work equal to $2T_0$ will have been obtained, and an amount of heat equal to $\frac{PL}{n}$ taken from T_0 to T_1 . Now it follows from the second law of thermodynamics that $dA = Q \frac{dT}{T}$, where dA equals the work and Q the heat involved in any process which takes place reversibly and with the production of the maximum amount of work. Substituting in this equation, the values obtained in the above case, we have $Q = \frac{PL}{n}$. For T we put the absolute freezing point of the solvent T_0 , and $dT = T_0 - T_1$, the lowering of freezing point, while the work accomplished equals $2T_0$.

Hence $2T_0 = \frac{PL}{n} \frac{T_0 - T_1}{T_0}$ or the lowering of freezing point $T_0 - T_1 = \frac{n}{P} \frac{2T_0^2}{L}$. Therefore the lowering of freezing point of a solution produced by 1 gram. mol. in 100 grms. of the

solvent, or the molecular lowering $\frac{M(T_0 - T_1)}{g} = \frac{0.02T_0^2}{L}$.

Since $n = \frac{g}{M}$, $T_0 - T_1$, equals the depression produced by g grams of a substance of molecular weight M dissolved in 100 grams of solvent.

2. MOLECULAR WEIGHT ESTIMATIONS BY THE RAISING OF THE BOILING POINT OF A SOLVENT.

This method has been founded on the relations discovered by von Babo (1848), Wullner (1856) and Raoult (1887) to exist between the vapour pressure of a solution and the amount of substance contained in the solvent.

Raoult found that equimolecular quantities of non-electrolytes, dissolved in a fixed amount of any solvent, depress the vapour pressure by a constant value depending only on the nature of the solvent. In the case of dilute solutions, the following relation between the concentration and the lowering of the vapour pressure was found to hold $\frac{p - p^1}{p} = \frac{n}{N}$ where p equals the vapour pressure of the solvent, p^1 that of the solution, and $\frac{n}{N}$ equals the ratio of the number of molecules of dissolved substance to those of the solvent.

The method used by the earlier investigators was to measure the lowering of the vapour pressure. It is to Beckmann that we are indebted for working out the method of determining the raising of the

boiling point, which is of much easier application.

For the calculation of the molecular weight we make use of the "constant of molecular elevation of Boiling Point" of the solvent employed, *i.e.*, the elevation of boiling point caused by the solution of 1 gram-molecule of the substance in 100 grams of solvent.

The constants K for various solvents are given :

			B.P.		K.
Water	100°	...	5.1
Ethyl ether	35°	...	21.6
Benzene	79°	...	26.1
Acetone	56°	...	17.1

These constants can also be deduced on thermodynamic grounds (*see page 15*), and are expressed by

$$K = \frac{0.02T^2}{q}$$

where $T = \text{B.P. on the absolute scale,}$
 $q = \text{latent heat of vaporisation.}$

If now, on dissolving S grams of the substance in I grams of solvent the boiling point is raised E degrees. The molecular weight is given by

$$M = K \frac{100S}{E.I.}$$

Practical. The following instructions must be carefully followed in order to make accurate measurements :—

Adjustment of the Thermometer. A thermometer similar to that used for the Freezing Point determinations is made use of. Since the interval

of temperature which can be measured by it at one time is limited to 4° or 5° , it must be set for each solvent according to the boiling point. This is effected as described in the section on the lowering of freezing point. The thermometer should be set so that the boiling point of the pure solvent lies somewhere between the 0° and 1° on the scale, thus leaving a sufficient interval for the elevations of temperature which will be measured.

*A. Method of Beckmann.** The annular vessel (*c.f.* Fig. 3) which serves to prevent radiation of heat from the boiling point vessel is filled to a height of 2–3 cms. with the pure solvent, two or three pieces of broken glass or porcelain being added to assist uniform boiling. The inner vessel which contains a thick piece of platinum sealed through its end, which ensures a formation of small vapour bubbles, is then removed and filled about 3–4 cms. high with small glass beads. The vessel is then suspended by wire to the balance and weighed to within 0.01 grm.; about 20 cc. of the pure solvent are now added, and the weight to within 0.01 grm. carefully noted. The thermometer is now fixed by a cork into the neck, so that the end of the bulb comes just above the level of the glass beads (the amount of solvent should be sufficient to cover the bulb of the thermometer). The two condensers, one for the annular vessel, and one for the boiling point vessel, are put into position, as shown in the diagram. The heating is effected by two small

* *Zeitschr. physik. Chem.*, viii, 223 (1891); xviii, 473 (1895).

Bunsen burners provided with screw clamps so that the flames can be accurately adjusted. The

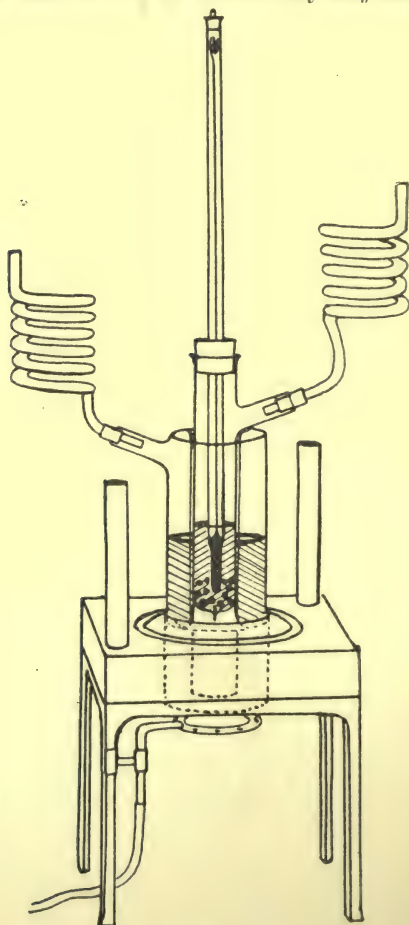


Fig. 3.

flames should be placed so as to be just inside—not quite under—the chimneys. In some cases a ring burner is provided in place of the above. The heating must be arranged so that from the condenser of the boiling point vessel a drop of liquid falls regularly about every 5—10 seconds. As soon as constant this temperature is noted as the boiling point of the pure solvent.

A small quantity of the substance, the molecular weight of which has to be determined, is now added; if a solid, in a compact form of known weight; if a liquid, from the previously weighed pipette with a long-drawn-out capillary, in either case care should be taken to touch the sides of the tube as little as possible. Four or five additions of substance are made, and the molecular weight calculated from each separate measurement. Determine the molecular weight of camphor in benzene solution by this method.

Take weights of camphor commencing with about 0.5 grm. and increasing by about 0.5 grm. each time for three times.

B. Method of Electrical Heating. A very convenient form of apparatus for molecular weight determination by the elevation of the boiling point method consists in raising the liquid to the boiling point by means of an electrically heated spiral of platinum wire immersed in the liquid. The tube is placed inside a Dewar vacuum flask to minimise radiation loss. The general arrangement of the apparatus is seen in Fig. 4. A current of about

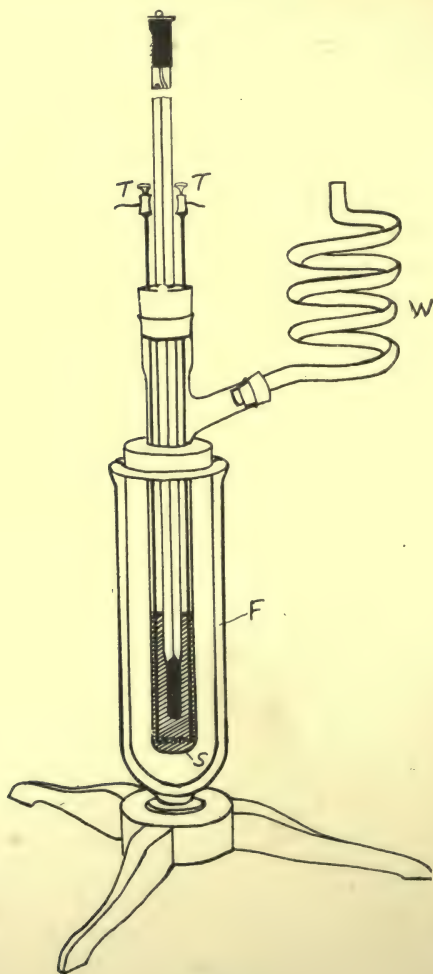


Fig. 4.

3 amps. at 4 volts is led from the terminal T along the copper leads to spiral S of platinum wire about .25 mm. thick, which is soldered to the ends of the copper leads. It is important, to ensure uniform boiling, that the wire spiral should be frequently coated with a layer of electro-deposited platinum, which is afterwards heated to a dull red heat. In this way, the evolution of small bubbles of vapour from the liquor is facilitated. A glass spiral is attached at W and serves to condense the vapour and allow the liquid to return to the tube. The solute is introduced at this side tube, and the whole experiment conducted generally as in the case of the Beckmann method.

[NOTE.] The relation between the elevation of Boiling Point and lowering of vapour pressure can be expressed as follows :
For small changes of vapour pressure

$$\frac{dp}{dT} = \frac{p(T_1) - p(T)}{T_1 - T}$$

where $p(T_1)$ and $p(T)$ represent the vapour pressures of the pure solvent at any two adjacent temperatures T_1 and T . Now let these temperatures denote the boiling point of the solution and pure solvent respectively. Then $p^1(T_1)$ the vapour pressure of the solution at its boiling point can be substituted for $p(T)$, so that

$$\frac{dp}{dT} = \frac{p(T_1) - p^1(T_1)}{T_1 - T}$$

$$\text{or } T_1 - T = [p(T_1) - p^1(T_1)] \times \frac{dT}{dp}.$$

Now every vaporization is governed by the thermodynamic relation first expressed by Clausius and Clapeyron,

$$q = T(v - v_1) \frac{dp}{dT}$$

where q denotes the latent heat of vaporization, v the volume in the gaseous condition, v_1 the volume in the solid (or liquid) condition, and p the pressure at the temperature T . The term v_1 may be omitted as being very small in comparison

to v , and we have $\frac{dp}{dT} = \frac{q}{vT}$.

Since $v = \frac{RT}{p}$ we have $\frac{dp}{dT} = \frac{qp}{RT^2}$.

Therefore

$$\frac{p(T_1) - p'(T_1)}{T_1 - T} = \frac{qp}{RT^2} \text{ hence } T_1 - T = \frac{p(T_1) - p'(T_1)}{p} \cdot \frac{RT^2}{q}$$

Now $\frac{p(T_1) - p'(T_1)}{p}$ the depression of the vapour pressure is equal to $\frac{n}{N}$, the ratio of the number of molecules of solute to solvent. Hence if S grams of solute are dissolved in 100 grams of solvent $T_1 - T = \frac{S}{100} \frac{RT^2}{q}$, where q is the specific heat of evaporation

The expression $\frac{RT^2}{100q}$, or $\frac{0.02T^2}{q}$ is usually denoted by the value K .

3. DENSITY OF A GAS.

The density of a gas at N.T.P. is estimated by finding the weight of a known volume and dividing by the weight of an equal volume of air, which is free from carbon dioxide and water vapour, under the same conditions of temperature and pressure. For this purpose, a glass vessel is provided with two openings, a plain tap at a , Fig. 5, and a side tube at b . The tube c is sealed to the barrel of the tap, and can be connected with b by rotating the barrel. Two methods can now be employed for calculating the density of the gas:—

(1) The flask is weighed when full of air, which is dry and free from carbon dioxide, then exhausted and weighed again, and then filled with the gas in question, and a third weighing made. If m_0 is the weight of the vacuous flask, m when full of

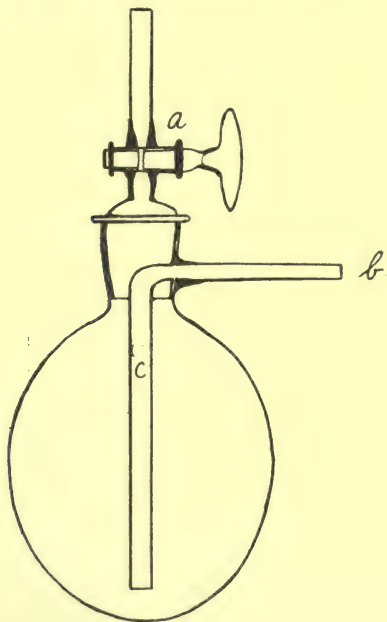


Fig. 5.

air, and m_1 when full of the gas, then the density of the gas is given by $\sigma_1 = \frac{(m_1 - m_0)\sigma}{m - m_0}$

If the temperature and pressure have remained the same during the different weighings, then for

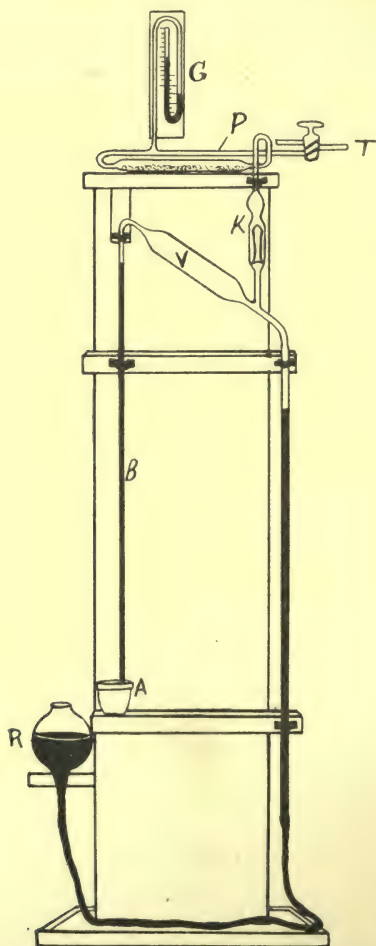


Fig. 6.

σ , the density of air, we may put 1, and σ_1 will correspond to the density of the gas at N.T.P.

(2) The second method consists in weighing the vessel when filled with the gas, with air, and with water, respectively.

In this method, the flask can be filled with the gas by displacing the air.

Let W denote the weight of water (or mercury) contained by the vessel, D the density of the liquid, and, as before, m the weight of the flask when full of air, and m_1 when full of gas.

If A is the actual weight of the air, G that of the gas, then $\sigma_1 = \frac{G}{A}$.

Now $G - A = m_1 - m$: $\therefore G = m_1 - m + A$, or $A = \frac{W\sigma}{D}$. $\therefore \sigma_1 = \frac{G}{A} = \frac{m_1 - m}{A} + 1 = \frac{m_1 - m}{W} \frac{D}{\sigma} + 1$.

The air displacement of the bulb has not been taken into consideration in this formula when weighing with water. The weight of water (W) can be corrected for air displacement by multiplying by 1.001, and the expansion between 4° and 16° may be corrected for, by again multiplying by 1.001.

During the weighing of the flask, it is advisable to use an exactly similar vessel, which is kept closed, as a counterpoise. In this way, compensation is made for slight variations in temperature and pressure and for changes in the humidity of the air, which affects the amount of water condensed on the surface of the glass.

The vessels should always be allowed to stand

in the closed balance case for a considerable time, until the weight remains constant. A rough balance can be used for weighing the water, as an accuracy beyond 0.01 gram is not needed in this case. The vessel can most conveniently be evacuated by a Töpler pump, an improved modified form of which is shown in Fig. 6. The vessel to be exhausted is attached to the tube T.

By raising the mercury reservoir R, the gas in V is driven down the capillary tube B, and out through the vessel A, containing mercury and into the atmosphere. By repeatedly lowering the mercury until V is again in connection with the apparatus and again displacing, the pressure can be reduced to any desired amount. The valve K prevents the mercury from rising above this point on raising R.

The phosphoric anhydride tube P takes up any water vapour present.

The pressure, when reduced to a few cms., is read on the vacuum gauge G.

When filling the flask with gas or air for density measurement, care must be taken that these are dry, and, in the case of air, free from carbon dioxide.

4. DENSITY OF A LIQUID BY THE PYKNOMETER.

The density is one of the most important constants in determining the purity of any definite

liquid substance, and in characterising any new chemical compound.

This method of determining density depends upon weighing a vessel full of the liquid and then weighing the same vessel filled to the same extent with water. It is capable of giving extremely accurate results if proper precautions are taken.

The Sprengel form of Pyknometer which is

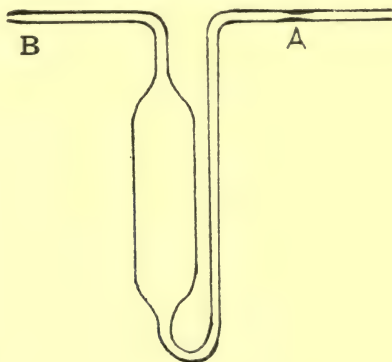


Fig. 7.

used for this purpose consists, as shown in Fig. 7, of a glass—or better fused silica—U tube one limb of which has a capillary bore, whilst the other is widened out and holds the greater part of the liquid.

A mark or constriction A on the horizontal end of the capillary tube denotes the point up to which the tube has to be filled. The filling is carried out by inclining the tube and immersing the end

in a small bottle or beaker which contains the water or other liquid required for the experiment. At the end A, a piece of rubber tubing is attached and liquid is drawn into the tube so that it fills the vessel to more than the mark A. The tube is now brought into the upright position so that the arms A and B are horizontal, and is immersed in a water bath at some constant temperature, say 18° , after it has remained long enough to take the temperature of the bath (in all cases this temperature must be noted) the liquid can be withdrawn from the capillary end by touching with filter paper and is adjusted accurately to the mark A. The Pyknometer is then carefully dried on the outside and weighed as accurately as possible on a delicate balance.

The process described above must be carried out with the tube filled first with water, then with the liquid the density of which is required. The accurate weight of the empty and dry Pyknometer must also be determined. The tube can be dried by drawing air through it after it has been well heated in an air oven, or else over a Bunsen flame.

It is essential that the temperature of the water bath in which the tube is immersed should be exactly the same in the case of the water as in that of the liquid experimented with.

With a vessel holding 5 cc. results accurate to ± 0.0001 should be obtained.

THERMO-CHEMICAL MEASUREMENTS.

5. HEAT OF NEUTRALISATION.

Prepare 250 cc. each of half normal or of normal sodium hydrate and hydrochloric acid (or sulphuric acid) and determine accurately their strength. The caustic soda must be as free as possible from carbonate and therefore should, before being standardised, be treated with a little solid barium hydrate, and afterwards kept well corked.

Two calorimeters, complete with covers, and two thermometers, whose readings have been compared with each other, are required. In one calorimeter is placed the metal vessel in which the reaction is to be carried out, and which should rest on a thin disc of cork. A measured quantity of the standard alkali should be poured in, and one of the thermometers inserted. An equivalent quantity of the acid is placed in a small glass flask in the second calorimeter together with a thermometer. The two solutions should be brought to approximately the same temperature and the temperature of each read at intervals for a few minutes. As soon as the temperature of each is constant or changing at a uniform rate, the flask containing the acid is removed from its calorimeter and the contents poured rapidly into the metal vessel containing the alkali. The liquid is stirred with the thermometer and again temperature readings are made.

In such cases as the above, where we are dealing with the heat of reaction between an acid and a base, the heat change is very rapid, so that usually no allowance has to be made for the loss through cooling. In cases where the maximum temperature is not immediately attained, however, readings must be taken at intervals of one half minute and continued until the fall of temperature becomes very regular. The cooling loss has then to be calculated by the method described below (p. 38).*

The heat changes of the solutions can be represented diagrammatically as shown by the curves in Fig. 8; *a* here represents the tempera-

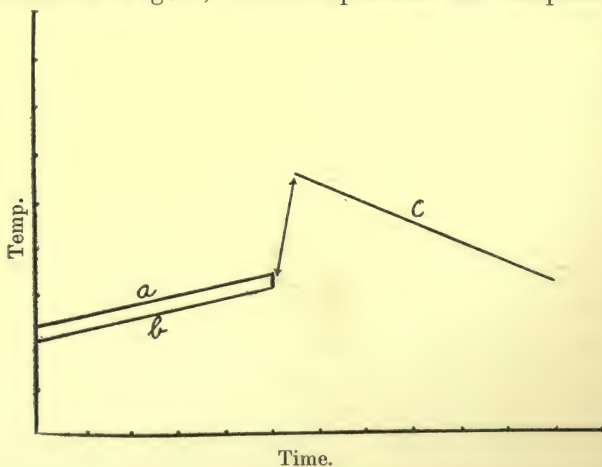


Fig. 8.

* See also Schuster and Lees' "Exercises in Practical Physics," p. 126.

ture of the acid, b that of the base, and c that of the mixed solutions.

If q is the quantity of heat in calories of the chemical reaction, A the specific heat of one solution, B of the other, t the final temperature (maximum, corrected), ta and tb the initial temperatures (corrected), b the water equivalent of the calorimeter with thermometer, etc.,

$$\text{then } q = A(t - ta) + (B + b)(t - tb).$$

For A and B , we may take the specific heat of the same volume of water as the solution measured. So far as b is concerned we can calculate the water equivalent of the calorimeters from the weight of the vessel, multiplied, in the case of platinum, by 0.0320 and in the case of copper by 0.093, the respective specific heats of those metals.

For the water equivalent of the thermometer, since we do not know the relative weights of mercury and glass of which it is constructed, we can make use of the fact that, volume for volume, mercury and glass have about the same specific heat, *i.e.*, 0.47 per cc. The volume of the thermometer immersed can be measured by inserting in a narrow measuring cylinder or inverted burette partially filled with water, and finding the displacement.

In place of the ordinary form of calorimeter, great accuracy can be obtained in these thermochemical measurements by the use of a Dewar vacuum cylinder in which the heat losses to the surroundings are minimised.

The water equivalent of the mixing vessel must of course first be ascertained. This is most conveniently done by adding a known weight of warm water, and finding the fall in temperature, or else by adding a weighed solid body, of known specific heat and heated to a definite temperature, to the flask containing a known amount of water and noticing the change in temperature.

In accordance with the theory of electrolytic dissociation, the heat of neutralisation of any completely dissociated (strong) acid with any dissociated base is a constant, since, in these cases, the sole reaction consists in the union of the H^+ and OH^- ions.

6. DETERMINATION OF THE CALORIFIC POWER OF GASES BY MEANS OF JUNKERS' CALORIMETER.

The apparatus of Junkers' has been designed for determining the heating power of gases, and is constructed on the following principle.

The gas is burnt in a special burner which is placed in a space surrounded by a jacketed vessel through which water is kept flowing. The vessel is so constructed that practically all the heat given off by the burning gas is absorbed by the water.

Measurements (1) of the amount of gas burning, (2) of the rate of flow of water through the jacketed vessel, and (3) of the difference in the temperature of the water on entering and on leav-

ing the apparatus, enable us to calculate the heating power of the gas.

The construction of the calorimeter can be seen from Fig. 9.

A flame (A) is introduced into a combustion chamber formed by an annular copper vessel, the annular space being traversed by a large number of copper tubes connecting the roof with the bottom chamber (B).

The heated gases circulate inside the tubes from the top to the bottom, whilst a current of water ascends outside the tubes in the opposite direction.

By means of this arrangement of counter currents, all the heat produced by the flame is transferred to the water and the spent gases escape through the throttle at atmospheric temperature.

The pressure of the water current is kept constant by two overflows (C) and (D), and the quantity of water passing through the apparatus can be regulated by the stopcock (E). A baffle plate (F) surrounds the lower end of the tubes to ensure an even distribution of the water, and in the neck of the apparatus, at (H) several discs with cross slots are arranged to ensure an intimate mixture of the heated water before it reaches the thermometer.

Provision is made to collect the water which is formed during the combustion of the gas in the annular space (K) and to pass it into a measure glass through the tube (L).

To prevent radiation the whole body of the apparatus is enclosed in an air jacket formed by a

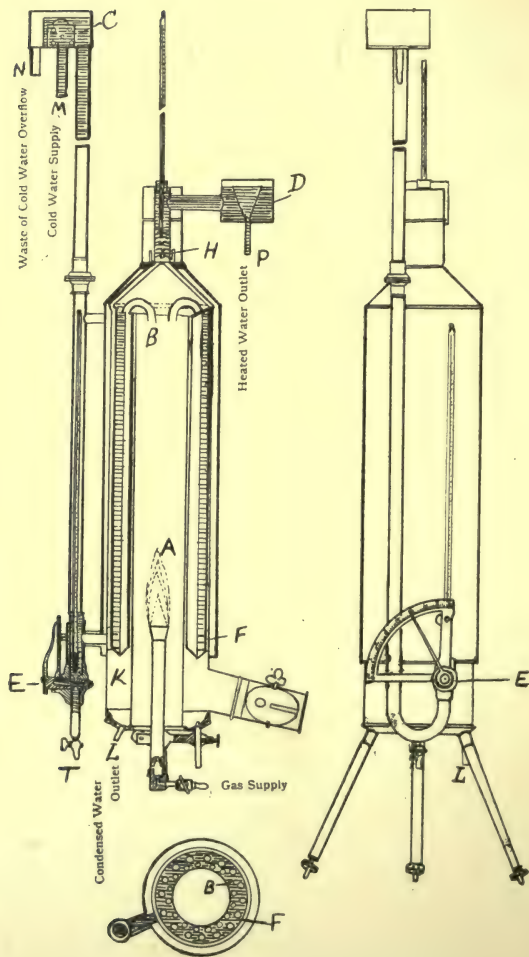


Fig. 9.

nickel-plated copper cylinder. As the standard unit of heat, the Calorie, is used (*i.e.*, the amount of heat required to raise the temperature of 1 kilo (1 litre) of water 1°).

If British Thermal Units are required, the result in Calories has only to be multiplied by the factor 4 (more correctly 3.968).

The following apparatus is required:—

(1) A water supply capable of passing from 1 to 3 litres per minute.

(2) A correct experimental gas meter calibrated to pass $1/10$ cubic feet for one revolution of the large index pointer.

(3) Two graduated measuring glasses 100 cc. and 1 litre.

It is advantageous to pass the gas through a gas governor to ensure even pressure during the tests.

The calorimeter is placed as shown in Fig. 9 so that one operator can observe the two thermometers of the entering and escaping water, while a second operator reads the index of the gas meter and at the same time reads the volume of water in the large measuring cylinder.

No draught of air must be permitted to strike the exhaust of the spent gas.

The water supply tube is connected to the tube (M) in the centre of the upper container; the other tube (N) is provided with a waste pipe to carry away the overflow. This overflow must be kept running while the readings are being taken, and in order to observe this, a short piece of glass tube may be inserted in the waste tube.

The tube (P), through which the heated water leaves the calorimeter, is connected by an india-rubber tube with the large measuring cylinder.

The smaller measuring cylinder is placed under the tube (L) to collect the condensed water.

After the thermometers have been placed in position with their indiarubber plugs, the water supply is turned on by the cock E, and the calorimeter filled with water until it begins to discharge at P.

At the end of the experiment, the calorimeter is emptied by the tap T.

Working the Calorimeter. For gases of high calorific power (*e.g.*, illuminating gas) the burner furnished with the calorimeter should be used, for gases of lower power (*e.g.*, hydrogen; carbon monoxide, Dowson or Mond gas) the plain metal tube serves as a burner.

The calorimeter has a maximum capacity of absorbing 2,500 calories per hour, the quantity of gas burned during the tests should therefore be regulated so that the flame produces only about 1,000 to 1,500 calories per hour. This will be the case if the respective gases were burned at the rate of the following quantities per hour:—

Illuminating Gas ... 4 to 8 cubic feet.

Hydrogen 8 to 16 cubic feet.

Dowson Gas 16 to 32 cubic feet.

Before beginning experiments, try whether the gas conduit from the meter to the apparatus is perfectly tight by opening the supply from the main, closing the taps on the burner, and observ-

ing that the indicating pointer of the meter remains stationary; then turn on the water, and fill the calorimeter until the water appears at the discharge tube, making sure that the overflow is working freely.

The burner must not be lighted until sufficient gas has been passed to displace all the air from the meter, etc., it must also be lighted outside the combustion chamber to avoid explosions of accumulated gas.

Insert the burner so that the flame is 5 or 6 inches above the lower edge of the apparatus. When the flame is burning and the water flowing the temperature of the water at the discharge will begin to rise; and, within a few minutes, the exit thermometer will remain approximately stationary.

The cock (E) regulates the quantity of water passing through the calorimeter. The smaller the quantity of water the higher will its temperature become. Ten to twenty degrees is the suitable rise in temperature to work with.

Taking the Readings.

When the pointer of the gas meter passes zero, or a whole figure, transfer the hot-water tube from over the waste into the measuring vessel and read and note down the temperature of the hot-water thermometer every half minute while the vessel is being filled.

The cold-water thermometer can be similarly observed, but will probably remain fairly stationary. As soon as the quantity of water

reaches some definite mark on the measuring vessel read the gas meter. The following readings will serve as an example.

Gas Meter.	Cold Water Thermo- meter.	Hot Water Thermo- meter.	Water.
5 cubic feet	8.77°	26.75°	
	„	26.70°	
	„	26.82°	
	„	26.80°	
	„	26.75°	
5.344 „ „	„	26.80°	2 litres

Gas burnt

0.344 cub. ft. 8.77° mean. 26.77° mean. 2 litres.

The following equation will give the heating value of the gas:—

$$H = \frac{W.T}{G}.$$

where H is the calorific value of one cubic foot of gas.

W is the quantity, in litres, of water heated.

T is the difference in temperature of the inflowing and outflowing water.

G is the quantity in cubic feet of gas burnt during the experiment.

In the example given $H = \frac{2 \times 18}{0.344} = 104.65$ Calories.

It should be observed that this is a “gross” value which represents the total heat generated by

the flame and includes the latent heat of the steam which condenses in the calorimeter and which is measured in the small cylinder.

This latent heat is not however, as a rule used in processes where gas is being burnt, so that the water which is formed escapes as steam.

Consequently, it is important to ascertain the "nett" value by deducting this value for the latent heat, which in many cases amounts to about 10% of the gross value.

To make this deduction, an allowance of 0.6 Calories must be made for every c.c. of the water condensed.

It is well to make a series of determinations of the gross calorific value for each 2 litres of water collected, and then to measure the water condensed throughout the whole series.

Supposing 2 cubic feet of gas condense 53 c.c. of water, we should ascertain the calorific value of the latent heat of the condensed water thus:—

$$\frac{0.6 \times 53}{2} = 15.9 \text{ Calories.}$$

which should be deducted from the gross value, leaving the nett calorific value equal to 88.75 Calories per cubic foot.

Some 4 or 5 determinations should be made, the gas being burnt at various rates between 4 and 8 cubic feet per hour.

The reading of the two thermometers used must be compared by placing together in a beaker of water at the same temperature.

7. HEAT OF COMBUSTION. MAHLER-COOK BOMB.

This is a modification of the Berthelot Mahler bomb and provides for the combustion of the substance under investigation in an atmosphere of oxygen under pressure in a steel vessel. By conducting the reaction in a suitable calorimeter, the rise in temperature produced enables the calculation of the heat of reaction.

Description of Bomb. This consists of an enamel-lined steel vessel capable of withstanding high pressures.

The cover A (Fig. 10) is screwed on to the lower part D and a gas tight connection is made by means of the lead spigot at C. Two stout platinum wires pass through the cover, one (T) being insulated from it by means of a quartz plug. The wires are connected to the two terminals and serve to lead the current to the connecting spiral of thin wire at S. One of the wires is bent round in the form of a loop so as to support a crucible which may be of platinum, porcelain, or silica. The spiral is arranged to touch the combustible solid, which can be ignited by fusing the connecting wire S, by the passage of an electric current.

Experiment. Open the bomb by unscrewing the large nut (B) at the top of the cylinder. Remove the cover, taking care not to bend the suspended wires, and place upright on an iron stand. Place the crucible, which has been carefully cleaned, in

BOMB CALORIMETER

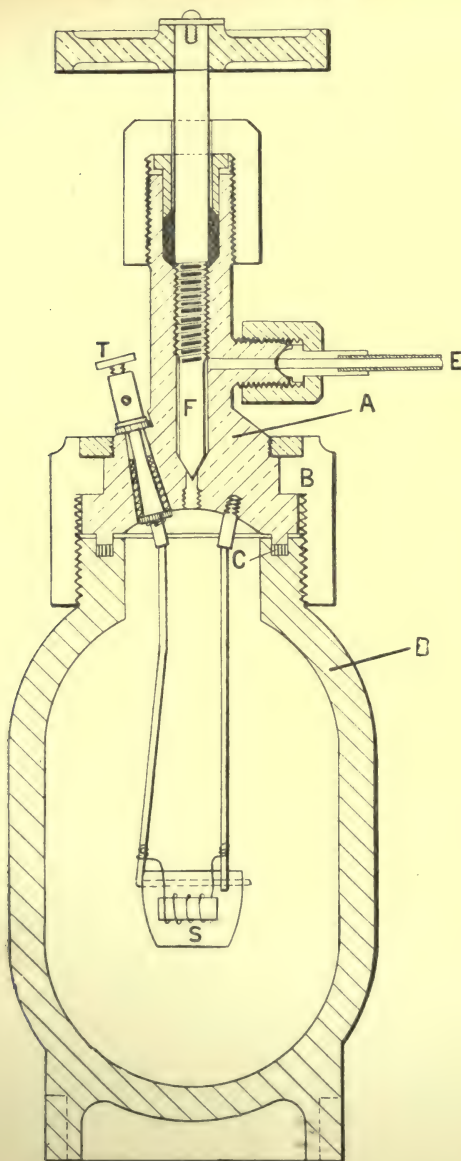


Fig 10

position in the ring of platinum wire. A piece of fine wire of platinum or iron, about 16 cms. long is made into a spiral by coiling it round a piece of glass rod. The spiral is then connected between the two pieces of thick platinum wire by twisting the ends round.

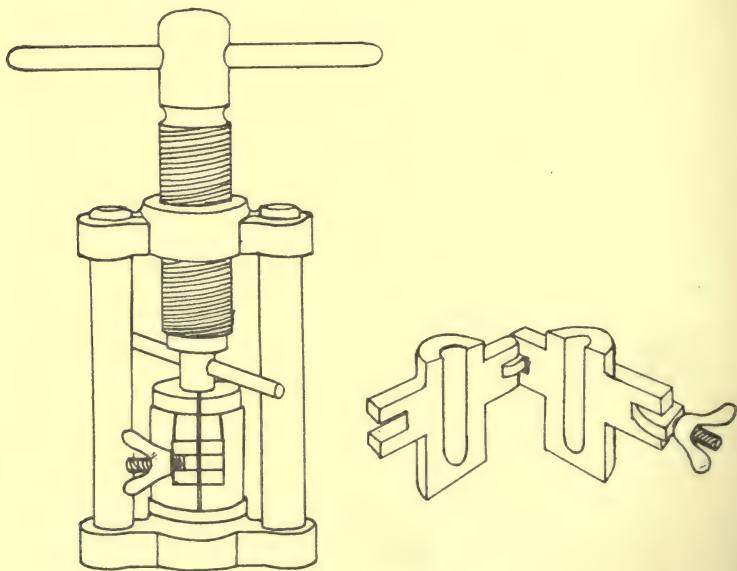


Fig. 10a.

By means of a special press, the combustible substance is compressed in the form of a cylinder. (In the case of hard substances like coal, the solid must be first finely powdered and then compressed.) A convenient form of press for this purpose is shown in Fig. 10a. The material is then weighed, about 1 gram being taken, and placed in a crucible. The

coil of wire is then pushed down on to it, and contact ensured. The cover is then placed in position, taking care that the ring of lead and the steel ridge are clean. Any lead which has been pressed out of the ring should be bent over again.

The nut B is then screwed down, the bomb being held by the bottom nut C in a hexagonal slot in an iron plate, and the nut B screwed up tight with a large spanner.

The bomb is then connected at E with an oxygen cylinder and pressure gauge. The valve screw F on the bomb is then closed. (*Force need not be used with this valve.*) The valve on the oxygen bottle is then opened *slowly* and cautiously (to avoid a sudden thrust of pressure on the gauge) until the pressure gauge shows that the gas is being emitted, when the valve F is opened slightly, and the gas allowed to enter slowly. When the pressure reaches 25 atmospheres, both valves are closed and the bomb disconnected. A leak can usually be detected by the sound.

The Calorimeter. The outer enclosure is filled with water at the temperature of the room, and 2.5 litres of water at about the same temperature, after being carefully measured, are placed in the calorimeter. This is dried on the outside and placed in the enclosure, where it rests on three pieces of cork.

The Beckmann thermometer—previously adjusted so that the mercury is near the bottom of the scale at the temperature of the water (see page 2)—is then placed in position in the calorimeter.

The stirrer is now set in motion and temperature readings are taken every minute.

When the temperature is quite steady or changing at a uniform rate, the readings are taken for another 5 minutes or longer.

At a known moment the charge is fired by closing the electrical circuit of about 20 volts by means of the plug key. Temperature readings are now taken every half minute until the fall of temperature has become quite regular, the stirrer being kept in gentle motion the whole time.

Immediately the experiment is finished, the bomb must be opened, taking care to first release the valve F to liberate the gas. The crucible is then examined to see if all the substance has burnt, and the bomb is then well washed out with dilute alkali and then with water. This precaution must be taken as soon as possible after the experiment in order to remove the nitric acid formed during the combustion, which, if left, will corrode the lining and roof of the bomb. After carefully drying the bomb, the crucible should be filled with calcium chloride and the cover replaced.

Correction of Temperature Readings for Heat Exchange with Surroundings.

The magnitude of the heat exchange with the surroundings is proportional to the difference of temperature between the calorimeter and the enclosure. The correction for this error is made in these experiments by noticing the change in temperature of the calorimeter before ignition has taken place (known as the first period), and then

after the combustion, an estimation is made of the change in temperature of the calorimeter after the maximum temperature has been reached. For this purpose, readings must be taken for about 5 minutes after the fall has become steady.

Readings should be made and entered as follows:—

First Period.

Time (mins.)	Temp.
0	0·953
0½	0·955
1	0·957
1½	0·958
2	0·960
2½	0·963
3	0·964
3½	0·966
4	0·969

Material Ignited. Second Period.

Time.	Temp.	Cooling in Interval.	Total Loss.
4½	1·5	−0·0001	−0·0001
5	2·1	+0·0010	+0·0009
5½	2·3	0·0015	0·0024
6	2·4	0·0016	0·0040
6½	2·45	0·0018	0·0058
7	2·47	0·0018	0·0076
7½	2·496	0·0019	0·0095
8	2·503	0·0020	0·0115
8½	2·508	0·0020	0·0135
9	2·510	0·0020	0·0155
9½	2·512	0·0020	0·0175
10	2·511	0·0020	0·0195

Third Period.

Time	Temp.	Cooling in Interval.	Total Loss.	Corrected Temperature.
10 $\frac{1}{2}$	2·510	0·0020	0·0215	2·5315
11	2·508	0·0020	0·0235	2·5315
11 $\frac{1}{2}$	2·507	0·0020	0·0255	2·5325
12	2·505	0·0020	0·0275	2·5325
12 $\frac{1}{2}$	2·504	0·0020	0·0295	2·5335
13	2·502	0·0020	0·0315	2·5335
13 $\frac{1}{2}$	2·500	0·0020	0·0335	2·5335
14	2·498	0·0020	0·0355	2·5335
14 $\frac{1}{2}$	2·496	0·0020	0·0375	2·5335
15	2·493	0·0020	0·0395	2·5325
15 $\frac{1}{2}$	2·490	0·0020	0·0415	2·5315
16	2·488	0·0020	0·0435	2·5315

The time and temperature columns are first filled in, and from these the rates of cooling in the first and third periods are estimated. In the above cases, these are respectively $-0\cdot002$ and $+0\cdot002$ degrees per minute, the negative rate of cooling denoting that the temperature is here rising. A straight line is drawn through the points at $-0\cdot002$ and $\cdot9$ and at $\cdot002$ and $2\cdot5$ (*c.f.* Fig. 11). From this curve, the cooling at intermediate temperatures can be estimated and the columns filled in. It is then seen that—

Corrected maximum temperature = $2\cdot531$

Initial temperature = $0\cdot969$

Rise in temperature ... $1\cdot562$

The heats of combustion of the following substances are given:—

Naphthalene	9668	calories	per	gram.
Camphor.....	9330	,	,	,
Iron (ignition wire)	1650	,	,	,

Experiment 1. Using naphthalene or camphor, determine the water equivalent of the bomb and calorimeter.

Experiment 2. Determine the heat of combustion of a sample of coal.

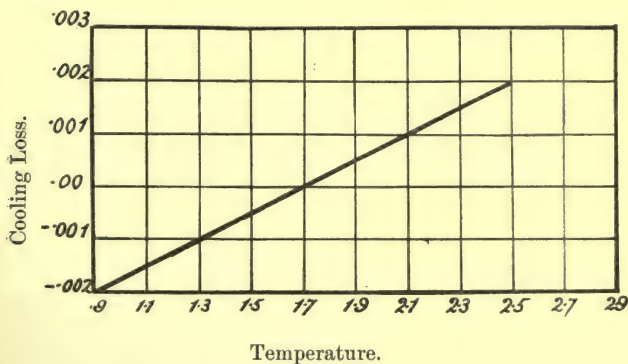


Fig. 11.

In exact measurements of calorific values, an estimation must be made of the amount of oxides of nitrogen formed during the combustion. An analysis of the residual gas must, for this purpose, be made, and the heat absorbed in the formation of the oxides of nitrogen allowed for.

8. CALIBRATION OF SLIDE WIRE BRIDGE.

METHOD OF STROUHAL AND BARUS.

Since no wire can be drawn of accurately the same diameter even if the material of which it is made is uniform, it follows that in the same lengths of wire the resistance will vary slightly from one case to another. For use in accurate electrical measurements it is necessary to know what corrections to apply. The difficulty of directly measuring the resistance of a short length

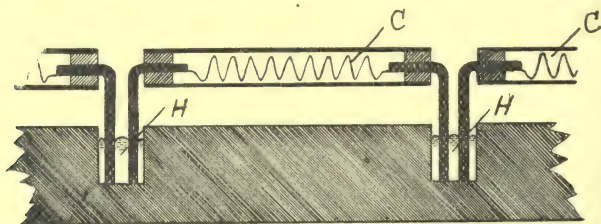


Fig. 12.

of wire in a middle of a long piece lies in the uncertainty of making a contact with other wires which shall be free from resistance. In the method of Strouhal and Barus, which is based on the Wheatstone Bridge principle, these contact resistances do not interfere with the measurement.

Ten approximately equal resistances are provided, the sum of which is about the same resistance as that of the wire to be calibrated. These resistances are in the form of wire coils (Fig. 12) soldered on to copper wires, for protection

they are mounted in glass tubes. The ends of the copper wire are amalgamated and dip into mercury cups (H) arranged on a long board (Fig. 13), which is placed parallel with the meter bridge (M). The end mercury cups are connected by copper wires (D) with the ends of the bridge. The method of calibration consists in finding lengths of wire at different positions along the meter bridge, which are of equal resistance.

For measurement we require a source of current

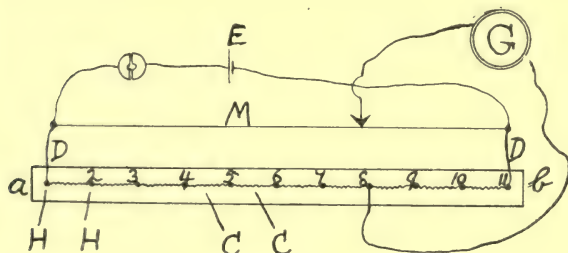


Fig. 13.

and an instrument for detecting when exact compensation has been effected. We may use either an induction coil and a telephone, or a storage cell and a sufficiently delicate galvanometer, *e.g.*, a simple astatic galvanometer.

The apparatus is arranged as shown in the figure, the source of current (E) being connected to the ends *a* and *b* of the bridge whilst the measuring instrument, (galvanometer G), is connected with the slider on the bridge and with the several mercury cups in turn as the experiment

proceeds. One of the resistances must be chosen as the standard and marked to distinguish it from the others, but it is of no importance which particular one is chosen.

The "standard" coil (V) having been placed between cups 1 and 2, the current connections are made and the measuring instrument wire placed in cup 2, and a point on the meter wire found at which no current passes.

The coil V is now interchanged with that between 2 and 3, and, without moving the galvanometer wire from 2, another reading is taken, the galvanometer wire is now placed in 3 and a reading taken. The difference between these last two readings corresponds to a length of the meter wire, the resistance of which is the same fraction of the total resistance of the meter wire, as V is of the sum of the ten resistances.

The coil V is now brought between 3 and 4, the readings taken with measuring instrument wire, first in 3, and then in 4, and a similar process continued until V has finally reached a position between 10 and 11, where only one reading is necessary, *i.e.*, with the wire in No. 10. By this means, the wire has been divided up into ten lengths of equal resistance and which are each approximately a tenth of the total length of the wire (column 3 in table below). These ten lengths are added together, the difference of the sum from 1000 mm. divided by 10 and each single value corrected by this amount, so that now the sum of the ten is exactly 1000 mm. (column 5). If

these single corrected values are now added as follows: 1, 1+2, 1+2+3, we obtain points which correspond to successive tenths of the wire (column 6), and the difference of these values from 100, 200, 300, etc., as shown in column 7, are the corrections to be applied at the corresponding places.

EXAMPLE.

Left hand.	Position of Sliding Contact corresponding to end of "Standard" Coil at	Right hand. mm	Lengths of equal resistance.	Difference Correction.	Corrected lengths of equal resistance.	Sum of equal resistances.	Correction at end points.
Terminal		98.2	98.2	-0.27	97.93	97.93	+2.1
99.3		200.1	100.8	-0.27	100.53	198.46	+1.5
201.5		302.6	101.1	-0.27	100.83	299.29	+0.7
299.4		400.2	100.8	-0.27	100.53	399.82	+0.2
400.8		501.7	100.9	-0.27	100.63	400.45	+0.4
500.3		598.3	98.0	-0.27	97.73	498.18	+1.8
600.7		699.5	99.8	-0.27	99.53	597.71	+2.3
700.2		801.2	101.0	-0.27	100.73	698.44	+1.6
798.1		900.3	102.2	-0.27	101.93	800.37	-0.4
900.1	Terminal	99.9	99.9	-0.27	99.63	1000.00	—
Sum of equal lengths			1002.7		1000		

9. CALIBRATION OF AN AMMETER BY MEANS OF THE WATER VOLTAMETER.

The measurement of an electric current, so far as the *quantity* of electricity carried by it is concerned, can be determined by measuring its

chemical effects. Faraday was the first to measure accurately the chemical change, and to show that the same quantity of electricity always has the same chemical effect when the same chemical process is considered; and further, that when the same current produces chemical changes in more than one process these effects are proportional to the chemical equivalents concerned in the different processes.

An electrolytic cell arranged with a view to its use as an instrument for measuring electric currents is called a voltameter; those most commonly in use being the copper, silver and so-called water voltameters. The water voltameter consists really of an acid or alkaline electrolyte, which, on electrolysis, gives the hydrogen and oxygen in the same proportions as they are present in water. Such electrolytic processes are chosen for voltameter purposes, which proceed as simply as possible and in which therefore the secondary reactions, which generally occur at the electrodes, are as little developed as possible. With the water voltameter these secondary reactions are sometimes rather marked and precautions must be taken for obtaining accurate results. For example, when a sulphuric acid solution is electrolysed, instead of the process proceeding simply and giving 1 volume oxygen to 2 volumes hydrogen, we may get persulphuric acid and ozone formed, both of which lessen the volume of oxygen evolved. It is therefore necessary to choose carefully the proper conditions of current density, temperature, con-

centration and nature of electrolyte to lessen the secondary reactions as much as possible.

The water voltameter due to Oettel consists of a small cell with concentric nickel electrodes, the electrolyte being 15 per cent. sodium hydrate. In this cell, only with high current densities, *i.e.*, large current in proportion to electrode surface, is there likely to be any discrepancy due to secondary reactions.

In order to calibrate the ammeter, it is placed in series with an adjustable resistance and with the water voltameter, so that the same current passes through the whole circuit, the smaller internal electrode should be made positive and on it the oxygen is evolved.

From five to ten points on the ammeter scale should be calibrated, two separate determinations of each reading being taken.

For the low readings, a small eudiometer can be used, but for the larger values it is better to collect a larger volume in a measuring cylinder.

Correct each gas reading to N.T.P. allowing for the pressure of the water vapour.

In order to obtain accurate and concordant results the volume of gas collected should not be too small, so as to reduce as much as possible the errors in the time measurement. One Amp. minute gives 10.44 cc. electrolytic gas (at N.T.P.).

Tabulate results as follows:—

Reading. Amps.		Current calculated from gas evolved. Amps.
·1	·095
·25	·245
·50	·518
1·25	1·325
1·50	1·590
1·75	1·86
2·00	2·20

The current must be kept constant during any particular measurement.

A curve constructed from such a series of readings and corrections would enable the ammeter to be used for accurate experiments.

10. CHARGE AND DISCHARGE OF AN ACCUMULATOR.

Theoretically any reversible cell can be used as an accumulator of electrical energy. For instance, in an ordinary Daniell cell, consisting of copper in copper sulphate, and zinc in zinc sulphate solution, when current is taken out, a solution of the zinc and deposition of the copper occurs, while, if a current is passed through it in the opposite direction, it is brought back to its initial condition by the redissolving of the copper and the deposition of the zinc. In such cases, we can store up and mutually transform electrical into chemical energy.

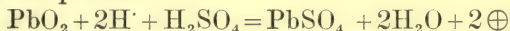
The form of accumulator which is in most general use at the present time is based on the changes which metallic lead and its compounds undergo in dilute sulphuric acid by the action of the electric current. The simplest form of such an accumulator, the discovery of which we owe to Gaston Planté, consists of two lead plates, one of which is covered with spongy lead and the other with lead peroxide; both are immersed, a short distance from one another, in dilute sulphuric acid. The many types of cells differ principally in the manner in which these "active masses" of spongy lead and lead peroxide are produced and retained on the electrodes.

The change which takes place in the accumulator during charge and discharge can be expressed by the following simple equations.

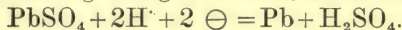
During discharge, at the negative plate—



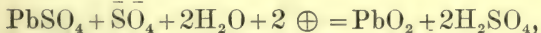
At the positive—



While during charge we have, at the negative—



at the positive—



and thus, when the charging current has acted for sufficient time, we shall have a complete recovery of the cell to its initial state, after which the passage of any further current will simply cause the evolution of hydrogen at the negative, and oxygen at the positive pole.

It will be noted that, as current is being taken from the cell, the sulphuric acid is more and more used up with the formation of lead sulphate, and that, by the recharging of the cell, the concentration of the acid is restored.

Charging of the Cell. In practice, the cells are constructed with each positive plate (PbO_2) placed between two negative plates (spongy lead), and as with the larger cells, where there are often several positive plates in parallel and several negative plates in parallel, it will be found that the number of negative plates is always one more than the number of positive plates. As an electrolyte, sulphuric acid of about 20 per cent. (1.15 specific gravity) is employed. The E.M.F. of the cell varies with the strength of the acid, being higher with a more concentrated solution. At a certain strength, however, the acid begins to attack the spongy lead with evolution of hydrogen. It is very essential that the acid should be quite free from any metal more electro-negative than lead, such as platinum. The smallest trace of such metallic impurities seriously impairs the action of the cell. This is caused by the separation of the metal on to the surface of the lead and the formation of a short circuited local element causing the lead to pass into sulphate. Further, the "over-voltage" effect (see p. 101), which plays an important part in preventing the evolution of hydrogen and oxygen, is diminished or destroyed by the smallest trace of certain metals.

For the purpose of charging, the positive pole

of the source of current is always connected with the positive of the cell.

The cell is taken to be completely discharged when its voltage has fallen to 1·8. If allowed to fall below this, the lead sulphate is slowly transformed into a hard crystalline condition which can only very slowly—or not at all—be retransformed into the metallic spongy lead.

During the charging, the voltage of the cell quickly rises to 2·1, and then slowly to about 2·3, which is the E.M.F. when completely charged, hydrogen and oxygen being given off at this stage on continuing to pass in current.

Capacity of the Cell. A knowledge of the capacity of the cell for storing electric energy is of great importance and can be easily determined by fully charging, and then discharging the cell, by allowing the current to pass through an ammeter and copper voltameter until the voltage has fallen to about 1·8.

The product of the amount of current in ampères by the length of time in hours gives the capacity of the accumulator in ampère hours. The rate of discharge must be noted, as the capacity varies somewhat with the rate at which current is supplied to, or taken from, the cell.

Maximum Rate of Charge and Discharge. The good preservation of an accumulator depends chiefly upon never discharging it below the point at which its voltage has fallen to about 1·8, and also upon never taking too large a current from the cell, since this is liable to cause a disintegra-

tion of the plates. The makers always give data as to the maximum current allowable for charging and discharging the cell, and care should be taken never to overstep this limit. If a larger current is required several cells should be used in parallel, in which case the maximum current is the sum of those individually permissible.

[NOTE.] In general, if we have n cells, each of E.M.F. E and normal discharge rate C , then, by arranging in parallel, we can obtain the current nC amps. at the voltage E ; by placing in series, we get the current C at the voltage nE . If we place n_1 in parallel and n_2 in series where $n = n_1 n_2$, we obtain the current $n_1 C$ amps. at $n_2 E$ volts.

Practical. Taking two small pieces of sheet lead, immerse them in dilute (about 20 per cent.) sulphuric acid, and pass a current between them of about .05 ampère per square cm. surface of positive or negative electrode. The plates should be connected with a voltmeter and the potential difference noted. Upon breaking the circuit, it will be observed that the two plates show a potential difference of about two volts, and that the anode is covered with a film of brown lead peroxide.

The charging and discharging of a small portable accumulator should be carried out in the following manner.

The type provided has a capacity of about 14 ampère hours, the maximum discharge rate is 1.5 amps., and the charging current 1 to 2.5 amps.

First of all arrange the cell with a regulating resistance and ammeter in circuit, and a voltmeter arranged to show the voltage of the cell, and charge with a current of about 2 amps. until gases are given off in considerable amount at the electrodes. Note the maximum E.M.F., both when the current is passing and when the circuit is broken. Now connect the fully charged cell with a regulating resistance, ammeter, and copper voltameter, and determine its capacity, from the copper deposited, by discharging until the E.M.F. has fallen to 1.8 volts, the current being regulated to about 2 amps.

The voltameter is constructed by taking three copper plates, one plate as cathode in between two plates which are connected by a wire and made the anode. The plates are placed in a rectangular jar which contains an electrolyte consisting of—

125 grms. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	}
50 grms. H_2SO_4	
50 grms. alcohol	
1 litre water.	

When the accumulator is fully charged and when it is discharged, the specific gravity of the acid should be measured by means of a hydrometer and the result noted.

During the charge and discharge the voltmeter should be read at intervals on both open and

closed circuits and curves drawn as shown in the diagram (Fig. 14).

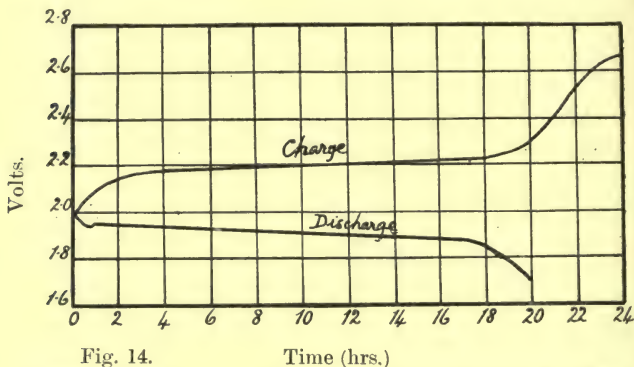


Fig. 14.

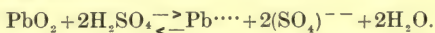
Time (hrs.)

[NOTE.] The voltage measurements for this table should be made by momentarily breaking the circuit and immediately reading the voltmeter on open circuit. With a closed circuit, the pole potentials, according to Ohm's law, will be given by $K = E + IR$, where E is the E.M.F. of the cell, I the current passing, and R the resistance. During discharging $K' = E - IR$. The difference in the pole potentials, as shown above, during charging and discharging, is due to the change in the acid concentration around the electrode. During charging, acid is liberated, and, during discharging taken from the pores of the electrode material. The diffusion of acid from or into the main bulk of the electrolyte being slow, changes in potential are caused by the change in acid concentration.

The difference between charging and discharging voltage (measured as above on open circuit) increases with increasing strength of current and converges towards zero with decreasing strength.

The mechanism of the reactions which take place at the electrodes has been represented by Le Blanc (*Zeit. Elektroch.*, vi, 48) as follows:—

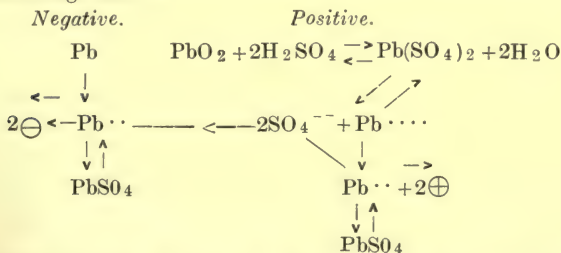
At the positive electrode, the peroxide forms tetravalent lead ions as follows :—



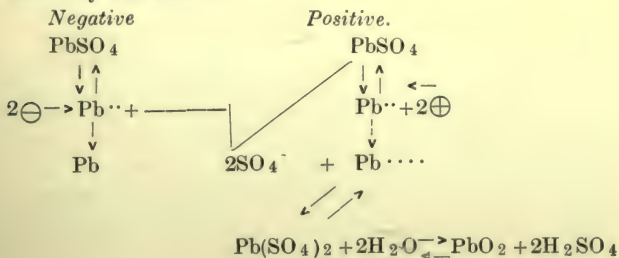
During discharging, the tetravalent lead ions give up two charges to the electrode and combine with one SO_4^{--} ion of the sulphuric acid to produce solid sulphate. At the same

time, at the negative electrode, one SO_4^{--} ion is discharged and forms PbSO_4 with the spongy lead. During the charging of the cell we have conversely at the positive pole, the bivalent lead ion $\text{Pb}^{\cdots\cdots}$ changed into the tetravalent ion $\text{Pb}^{\cdots\cdots}$ by taking up two charges from this electrode and then reacting with water to form lead peroxide. At the negative electrode the $\text{Pb}^{\cdots\cdots}$ ions pass into the metallic state by giving up their charge.

The complete reaction, during charge, is expressed by the following table :—



and conversely, during the discharge the reaction is represented by the table :—



Liebenow [*Zeit. Elektroch.*, ii, 420, 653 (1895)], developed a somewhat different theory to explain the reactions taking place in the lead accumulator. This is based on the assumption that a solution of lead sulphate contains, in addition to $\text{Pb}^{\cdot\cdot}$ and SO_4^{--} ions, a certain quantity of PbO_2^{--} ions, formed by the union of $\text{Pb}^{\cdot\cdot}$ with O^{--} ions of the water, or else by hydrolysis, thus: $\text{Pb}^{\cdot\cdot} + 2\text{H}_2\text{O} = \text{PbO}_2^{--} + 4\text{H}^+$.

At the positive electrode, lead peroxide passes into solution as PbO_2^{--} , imparting two positive charges to the electrode. This then reacts with the H^+ ions of the acid as follows:—



The lead ions combine with the SO_4^{--} ions of the acid to form the solid sulphate:



At the negative electrode, the change consists in the passing of lead into the ionic condition and then combining with a SO_4^{--} ion to form solid sulphate as represented by the Le Blanc theory.

During charging, the reverse action occurs, i.e., at the positive pole, PbO_2^{--} ions, and at the negative $\text{Pb}^{\cdot\cdot}$ ions are precipitated from solution. The ions in solution are furnished by the PbSO_4 , accumulated at the electrodes.

11. ELECTRO-DEPOSITION OF METALS.

ANALYTICAL DETERMINATION AND SEPARATION OF METALS.

In a great number of cases, electrolytic methods of quantitative analysis possess advantages over the ordinary gravimetric methods, and, on this account, are coming into more general use. In some cases, much greater accuracy can be obtained with the electrolytic than with the gravimetric

method, and the manipulations are much simpler and quicker. The success of electrolytic estimations in practice depends chiefly upon being able to obtain coherent deposits of the metal, and in the case of separations, in being able to adjust the conditions for the complete deposition of one metal while others remain in the solution. In any case it is necessary to carry out the analysis under certain prescribed conditions. The strength of the current employed must in all cases be measured with an ammeter, the temperature maintained within certain limits, and, when effecting separations, the potential difference between the electrodes must be exactly adjusted. It is only under these conditions that one can be certain of obtaining the metal in a firmly adherent and smooth form, so as to enable subsequent washing and accurate weighing.

Apparatus. The apparatus devised by Classen consists of a light platinum dish A (Fig. 15) which is used as cathode. This is supported on a special stand which can be adjusted to any height. The anode (B) consists of a spiral of platinum wire, or else a perforated disc to allow the escape of the gases collecting on the under surface. In another form of apparatus, the cathode consists of a cone of platinum foil or gauze which is placed inside a beaker containing the electrolyte, and in the middle of the cone a thick platinum wire is suspended to serve as anode. A regulating resistance and a suitably graduated ammeter must be placed at R. in circuit with

the electrodes, so that the conditions of electrolysis can be adjusted and measured. The voltmeter V is connected across the electrode terminals.

In all cases of electrolysis, it is important to know the "current density" at the electrodes.

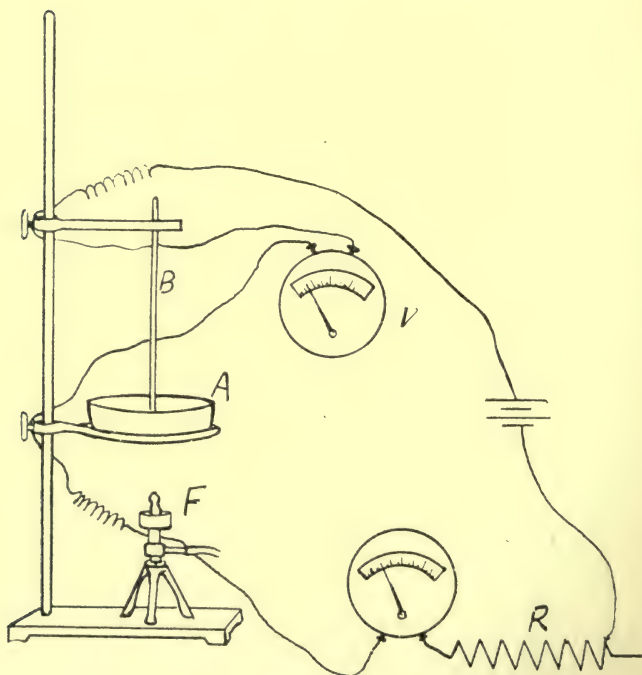


Fig. 15.

In the case of the deposition of metals, a definite current density at the cathode must be used. This is usually expressed in ampères per square

centimetre. It is consequently necessary to know the surface presented by the electrodes used.

Examples. The following cases are instances where electrolytic determinations can be carried out conveniently and with great accuracy.

Copper. Dissolve 1 to 1.5 gram $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, or any other copper salt (other than the chloride). Add 2 to 3 per cent. by volume of nitric acid. Electrolyse with a P.D. of 2.2 to 2.5 volts and current density 0.5 volts and current density 0.5 to 2 amps. per 100 sq. cms. Temperature of solution should be about 50° to 60° ; this is adjusted once for all before the beginning of the electrolysis by regulating the flame under the dish F (Fig. 15). The electrolysis vessel must be covered with a perforated watch glass to prevent loss by spurting.

The nitric acid becomes gradually reduced during the electrolysis, consequently it is sometimes necessary to add more acid from time to time with prolonged electrolysis.

The termination of the electrolysis can be conveniently determined by adding a little water to the dish so that the level rises 2 or 3 mm.; if no more copper is deposited on this new surface the electrolysis can be considered as finished. The solution should be finally tested by removing a drop and testing on a watch glass by adding excess of ammonia when a blue colour is obtained if any traces of copper remain.

When the electrolysis is finished, it is necessary to wash out the dish without breaking the current, otherwise the copper will redissolve in the nitric

acid solution. The liquid should therefore be syphoned off with a bent glass tube, while water is added so as to keep the electrodes covered, until the acid is too dilute to affect the copper. The dish is then rinsed out with a little more fresh water, and then with 2 or 3 cc. alcohol and dried at $80-90^{\circ}$ in an air bath, and then carefully weighed. An accuracy in the estimation to within 0.05 per cent. should be obtained.

This determination is specially useful in depositing copper in solutions containing metals of the iron group, since the latter remain dissolved in the nitric acid.

In technical analysis of copper or copper ores, arsenic and antimony are often met with and on electrolysis a portion of these elements is precipitated with the copper, giving it a brown colour.

This can be dealt with by weighing the dish and heating for some time over a Bunsen flame, thus volatilising the arsenic and antimony and leaving the copper in an oxidised condition. On redissolving in dilute nitric acid the copper can once more be electrolytically deposited, the difference in weight of the two deposits corresponds to the arsenic and antimony which had been thrown down.

Lead. The electrolytic method for the determination of lead possesses great advantages over the gravimetric methods usually employed, and is moreover of interest as the deposition takes place on the anode and in the form of lead peroxide. As anode a platinum dish with rough surface to

secure better adherence is employed, or else a wire gauze cathode. The solution should contain 10 per cent. free nitric acid.

P.D. 2·3—2·7 volts. Current density 1–2 amps. per 100 sq. cms. Temperature 50—60°.

The electrolysis is complete in about 1 to 2 hours.

The peroxide must be dried at 180—190° since it is deposited in a hydrated form.

Take 1—1½ grms. recrystallised lead nitrate, and estimate the percentage of lead.

The end of the deposition may be tested by taking a few drops of the solution on a watch glass, neutralising with ammonia, and then adding ammonium sulphide.

The dish or electrode is cleaned afterwards by adding hot *dilute* nitric acid, together with a few crystals of oxalic acid.

Nickel. There are two very satisfactory methods for determining this metal electrolytically.

(1) Take about 0·5 grms. Nickel as sulphate, with about 5 grms. ammonium sulphate and 6 cc. ammonia (0·880). Electrolyse with a current density of 0·5 to 1·5 amps. per 100 sq. cms.

P.D. 2·3—3·5 volts. Duration of electrolysis about 2 hours at room temperature.

(2) The second method, which is fully better than the first, is the one recommended by Classen.

Take 1·2 to 2·1 grms. $\text{NiSO}_4(\text{NH}_4)_2\text{SO}_4 + \text{H}_2\text{O}$, 4–5 grms. of ammonium oxalate, and 120 cc.

water. Temperature 60—70°. Current density 1 amp. per 100 sq. cms. P.D. 2·5 to 3·4 volts.

Nickel is conveniently estimated in presence of other metals as follows:—The acid solution is treated with sulphuretted hydrogen, when all the metals except nickel, iron, cobalt, zinc, manganese and aluminium can be removed. By treating the solution remaining (if necessary after conversion to sulphates) with ammonia—iron, aluminium and manganese can be precipitated, and the filtered solution is then ready for electrolysis. It is only when zinc is present that any special precautions have to be taken.

*Separation of Nickel and Zinc.**

A good example of the use of graded potentials is given in this case where a mixture of a nickel and zinc salt is being dealt with. In this case, the influence of temperature also plays a very important part as no separation can be effected below 50°.

Take about 0·12 grm. nickel and 0·15 grm. zinc as sulphates. Add 6 grms. ammonium sulphate, 30 cc. ammonia (s.g. 0·91) and 1 grm. sodium sulphite. Make solution up to 300 cc.

The temperature is adjusted to 90—92°, and a current density at the cathode of 0·2 amp. per 100 sq. cms. applied. When all the nickel is deposited, the cathode is weighed, cleaned, coated with copper (to prevent the zinc subsequently

* Hollard and Bertiaux, *Zeit. Elektroch.*, xiii, 565 (1907); *Chem. Ztg.*, xxxii, 185 (1908).

alloying with the platinum), again weighed, and the zinc deposited by using a current density of 0.6 to 1.0 amp. per 100 sq. cms., and conducting the electrolysis at the room temperature.

*Separation of Silver and Copper.**

A quantity of alloy up to 0.5 gram is taken and dissolved in 2 cc. nitric acid (1 in 4) diluted with water.

The solution is diluted to about 150 cc.; 5 cc. absolute alcohol are added which helps to prevent the silver being deposited as peroxide on the anode, as does also the warming of the solution to 55°. P.D. 1.36 ± 0.1 volt.

The analysis is rather a delicate one as the P.D. must not rise above the value given. After complete deposition of the silver, the electrolyte is removed, and after weighing and removing the deposited silver, the electrolyte is returned and the copper deposited in a similar manner by using a higher potential difference.

[NOTE]. The separation of one metal from another by electrolysis is rendered possible by the fact that different elements separate from solution at different potentials. The E.M.F. which has to be applied to cause the separation of any metal in a given electrolyte can be expressed by the formula $\frac{RT}{nF} \ln \frac{P}{p}$ where P is a constant for the metal, and represents its "solution pressure," while p denotes the osmotic pressure or concentration of the ions of the metal in solution, n denotes the valency, and F the number of coulombs (96540) associated

* Küster and Steinwehr, *Zeit. Elektroch.*, iv, 451.

with one gram equivalent. Taking for T the ordinary room temperature (19° *i.e.* 292° abs.), and dividing by 0.4343 to reduce from natural to ordinary logarithms, the above formula reduces to $\frac{0.058}{n} \log \frac{P}{p}$. From this, it is seen that in the electrolysis of a solution of a salt of a monovalent metal, a reduction of concentration from 1 gram of the salt in a given volume to 0.0001 gram, only makes a difference of 0.23 volt in the separation potential, and with a divalent metal only half this amount. Consequently, in many cases, where there is any considerable difference between the decomposition potentials of the two metals, a complete separation, within the limits of analytical detection, is possible. Of great importance is the selection of the electrolyte. In many cases complex ions are formed so that the concentration of the free metal ions is exceedingly small, and its decomposition potential correspondingly raised. Examples of this are seen in the case of copper, silver, and gold in cyanide solutions, where the ions CuCy_2 , AgCy_2 , AuCy_3 are formed.

RAPID ELECTRO-DEPOSITION.

On account of the low current density to which electro-depositions are limited under ordinary conditions, in order to obtain smooth adherent deposits of metal, electrolytic analyses are usually somewhat lengthy and often require several hours for completion. In many cases in analytical work this length of time demanded would be prohibitive to the practical use of the method. Electro-depositions can, however, be very much accelerated by making use of the following property. If means are taken to rapidly agitate the electrolyte during electrolysis, such as by rotation of the anode or cathode, the permissible current

density which is consistent with obtaining a good deposit can be very much raised. Thus, in the case of copper, while, under ordinary conditions, with stationary electrodes, the upper limit of current density is at about 0.02 amp. per square centimeter, ten to twenty times this amount may be employed by adopting suitable means to agitate the electrolyte, or rotate the electrodes. This effect is due to the fact that, by agitation, fresh electrolyte containing a high concentration of copper ions, is continually being brought into contact with the cathode, and also, when the cathode is rotated, some physical effect is produced which improves the smoothness of the deposit.

Practical. A simple form of apparatus which can be constructed to illustrate this method consists of a glass tube (A) (Fig. 16), down which a copper wire (B) passes. A constriction in the tube is formed at (C), and by running in wax, the space between the wire and the walls of the tube is here filled in. The copper wire (B) projects a short way above this seal, and, by means of mercury placed in the top part of the tube, enables an electrical connection to be established between the wire (D) inserted in the mercury and the copper wire. The copper lead terminates in a brush of fine wire at B, and from here, by contact with the inside surface, on to the platinum crucible which is fastened on to the cork E. A wider glass tube (F) surrounds the middle tube, and can be held in a clamp, after fitting an

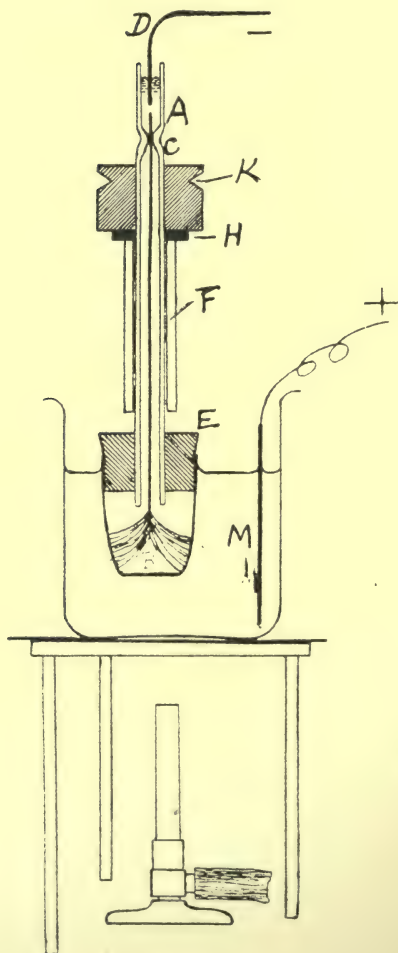


Fig. 16.

ebonite washer at (H), so as to permit the tube to be rotated with the minimum of friction. In order to rotate, a belt is fitted on to the grooved wooden cylinder at (K) which connects with a small motor. The platinum crucible is immersed in the electrolyte contained in a beaker, and an anode of platinum foil placed alongside at (M). The wire (D) dipping into a mercury cup forms the negative terminal. These terminals are joined in series with an ammeter and regulating resistance to the source of current, and while the cathode is rotating at high speed, the electrolysis proceeds as in the case with stationary electrodes. The temperature and composition of the electrolyte must be the same as in the former case. On completion of the electrolysis, the electrolyte must be diluted, and syphoned off before the circuit is broken. The beaker is then removed and the crucible with the copper deposit well washed, and finally rinsed with a few cc. of alcohol and dried, as in the case of the ordinary deposition of copper described above.

Others forms of rotating electrodes, in which a larger area of cathode is presented, are better suited in practice for electro-depositions than the above. The same effect is also obtained by rotating the anode instead of the cathode.

Experiment I. Measure approximately the outside surface of the crucible. Take ordinary (commercial) copper sulphate, dissolve in water and acidify with nitric acid (2-3 per cent. by volume). Arrange the cathode so as to rotate at

the highest possible speed without projecting any of the electrolyte from the beaker, and examine *qualitatively* the deposits obtained with different current densities.

Experiment II. Having found the highest current density with which a good deposit can be obtained, perform a quantitative experiment with pure recrystallised salt. Make notes of voltage, duration of experiment, etc.

12. QUANTITATIVE ESTIMATION OF NITRIC ACID BY ELECTROLYTIC REDUCTION TO AMMONIA.

The reduction of nitric acid, or of nitrates in presence of sulphuric acid can be brought about at the cathode during electrolysis. The product of the reduction depends on the nature of the metal of the electrode, thus if platinum is used, no ammonia is formed, so soon, however, as a copper salt is added to the solution and a deposit of copper thus caused to appear on the cathode, reduction commences, and almost the whole of the nitrate can be transformed into ammonium salt. A quantitative method of analysis has been founded on this process by Ulsch.*

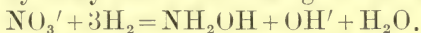
This reaction can be expressed by the equation



* *Zeit. Elektroch.*, iii, 546 (1897), cf. also Shinn, *J. Amer. Chem. Soc.*, xxx, 1378 (1908), and W. Bottger, *Zeit. Elektroch.*, xvi, 698 (1910).

in which one equivalent of acid gives two of alkali.

Another reaction which takes place with a copper cathode during electrolysis is the formation of hydroxylamine according to the equation



The relative proportions of ammonia and hydroxylamine obtained have been found by Tafel* to vary with the physical nature of the copper of the electrode, thus, using separated anode and cathode compartments, when a smooth copper cathode was used the reduction of nitric acid went to hydroxylamine to the extent of 11.5 parts, and to ammonia to the extent of 76.8 parts, while, with an electro-deposited copper surface, the product contained 1 part of hydroxylamine to 92.3 of ammonia.

In the electrolytic reduction of nitrates, the formation of hydroxylamine is accompanied by the production of the same number of equivalents of alkali as in the case of ammonia. Its formation, however, would cause an error in the result on account of its undergoing decomposition in presence of oxidising agents, which thus tends to give too low a value. A source of error which tends to bring the value rather high is caused by the fact that, during the washing of the electrode, a trace of copper tends to dissolve in the sulphuric acid which is present in excess. By carefully regulating the conditions of the electrolysis the formation of hydroxylamine can be made very

* *Zeit. anorg. Chem.*, xxxi, 289 (1907).

small, when the error caused by its presence is negligible, or is counterbalanced by the error resulting from the loss of acidity due to dissolved copper. The following method, which was worked by Ulsch, is used for the quantitative estimation of nitrates.

As cathode, a cylindrical spiral is employed; this is formed by winding a copper wire of about 1.4 mm. diameter on a tube about 15 mm. diameter, so that about 40 closely adjacent layers are present, the total length of wire being about 2 metres. At the end, 15 cms. of wire are left and bent in the direction of the cylinder axis so as to allow the connections to the source of current to be conveniently made. The spiral is very carefully drawn out so that a minute space is left between each layer and the total length of spiral cylinder is about 70 mms.

The anode is formed by a thin platinum wire which can be coiled round a glass rod to make rigid. This is arranged to pass down the centre of the copper coil. The cell consists of a glass tube, 2 cms. diameter and 17 cms. length, in which the electrodes are adjusted by means of a cork, which is provided with an outlet for the gases. The electrodes are carefully adjusted so that the platinum anode is fixed as the axis of the tube, surrounded by the spiral cylinder; both electrodes pass to the bottom of the tube.

Before each series of experiments the cathode must be covered with a coating of copper by electro-deposition, using a current density of at

least 2 ampères per 75 square cms. so as to obtain a surface of spongy metal. The surface can also be prepared by heating the wire to a red heat and quenching in water. It is on this condition of the metal that the complete reduction to ammonia and avoidance of the formation of hydroxylamine chiefly depends. After each experiment, the active surface of the electrode should be regenerated by heating in an oxidising flame and then quenching in water, or else by fresh electro-deposition.

As an example of the method, the following experiment with pure potassium nitrate should be carried out:—

Dissolve about 0.5 gm. potassium nitrate in a small quantity of water, add exactly 50 cc. normal sulphuric acid, and make solution up to 100 cc. with water in a measuring flask.

For each experiment take 20 cc. of this solution and add distilled water, if necessary, so as to cover the copper spiral.

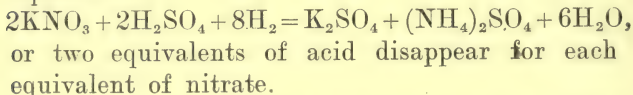
The electrolysis is carried out from a 4 volt circuit, using a regulating resistance, and a current density at the cathode of not more than 2 amps. per 75 sq. cms. surface. At higher current densities than this the formation of hydroxylamine begins to be appreciable.* During the electrolysis scarcely any gas will at first escape from the copper electrode, but later it will be found that hydrogen comes off abundantly. The reduction is almost complete before hydrogen is evolved in quantity,

* Cf. Böttger, *loc. cit.*

but the electrolysis should be continued for a further 10 minutes to ensure complete reduction.

By titration of the remaining acid, the amount of ammonia formed can be determined.

The complete reaction may be expressed by the equation—



An accuracy to within 0.1 per cent. is possible in this method of estimating nitrates.

13. MEASUREMENT OF ELECTROLYTIC CONDUCTIVITIES.

The determination of the electrolytic conductivity of solutions of salts, acids, and bases, has an important application in investigating the nature of solutions. The constitution of compounds can in many cases be ascertained by this method, and it enables the affinity of acids and bases to be accurately determined. The resistance of an electrolyte follows the same laws as in the case of a metal or solid conductor, in that the resistance is proportional to the length of the path of the current and inversely proportional to the cross section. This is expressed by the formula $R = r \frac{l}{f}$, where R is the resistance, l the length of the path of the electrolyte, f the cross section, and r is a constant depending on the nature of the

electrolyte. If l is expressed in centimeters and f in square cms., then r represents the *specific resistance*. The most important factors which determine the value of r are the concentration of the electrolyte, and the mobility of the ions.

Instead of r , its reciprocal $\frac{1}{r}$ is more commonly used, and this is known as the *specific conductivity*, and denoted by x . Thus $x = \frac{1}{r} = \frac{l}{wf}$ where w is the measured resistance.

The essential difficulty in the determination of electrolytic conductions lies in the fact that by use of a continuous current, such as is always employed in the electrolysis, polarisation occurs at the electrodes, and the actual resistance measured is the sum of the resistance of the electrolyte itself and of the polarisation at the two electrodes.

Kohlrausch was the first to propose the use of alternating currents, by means of which the polarisation caused by the passage of current in one direction is removed before it has had time to reach any appreciable magnitude, by the reversal of the current and its passage in the opposite direction. In this case the resistance measured is simply that of the electrolyte itself. For such work as this the alternating currents are best obtained by means of a small induction coil. The Wheatstone Bridge principle, exactly similar in nature to that already used for measuring metallic resistances, is made use of. To detect the point where equilibrium has been attained, use

is made of a telephone, which will emit a sound so long as any current is passing through, so that a minimum of sound will indicate that compensation has been effected.

Arrangement of the Apparatus. In Figs. 17 and 17a the induction coil is seen at S. The electrolytic cell W forms one arm of a Wheatstone

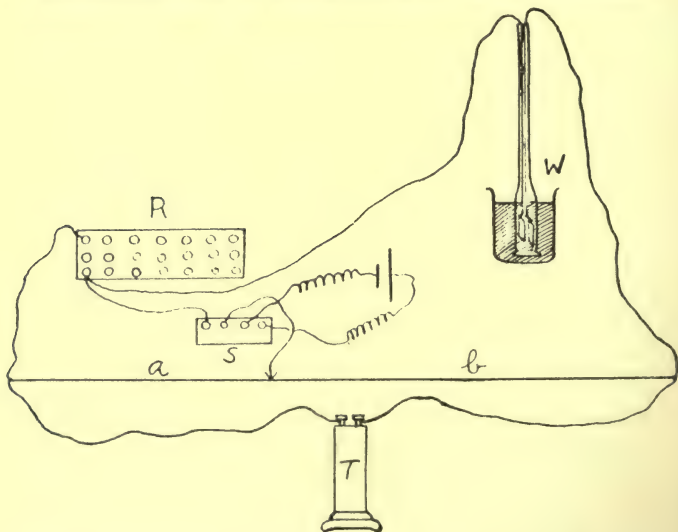


Fig. 17.

Bridge, the other arms being formed by the resistance box R and the two parts of the sliding wire bridge *a* and *b*. The connections are made as shown in the figure.

If *w* be the resistance of the electrolyte, R that taken out of the resistance box, and *a* and *b* the

two lengths of wire in the meter bridge when compensation has been effected, then $w : R = b : a$.

Hence $w = \frac{Rb}{a}$.

Electrolytic Cell and Solutions required. The most simple cell for measurements of this kind is formed by making use of a so-called "dipping

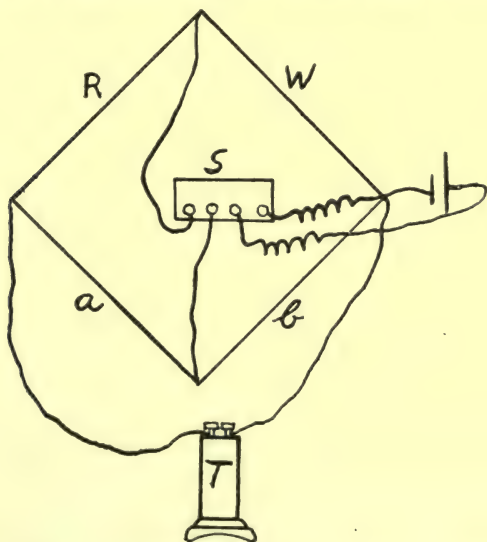


Fig. 17a.

electrode," which can be immersed in a beaker or tube containing the electrolyte. The dipping electrode consists of two small pieces of platinum foil, which have been carefully coated with platinum black or "grey" platinum. This platinised surface is prepared by electrolysis for a

few minutes a 3 per cent. solution of chloroplatinic acid, to which $1/40$ per cent. of lead acetate has been added. The current is passed through the electrodes, in opposite directions, for equal intervals of time, so as to coat both electrodes. After thoroughly washing, these platinised electrodes may be used for the measurements, or by heating to a dull red heat, the black platinum is converted into a grey deposit, which is still better suited for these measurements.

The electrodes of platinum foil are connected with leading in wires, and surrounded by a glass hood (W, Fig. 17).

Purity of Water. Particular attention must be paid to the purity of the water used in conductivity measurements. It must be carefully distilled, and the presence of dissolved gases (particularly carbon dioxide) must be eliminated. Perfectly pure water has been found to have a specific conductivity of 0.04×10^{-6} reciprocal ohms, at 18° . The conductivity of the water used in these measurements should be ascertained previously and should not amount to more than 20 times the above value.

Temperature Regulation. Since the conductivity varies very largely with the temperature, the beaker or tube containing the electrolyte must be immersed in a water bath or thermostat, the temperature of which can be regulated and kept constant to within $1/10^\circ$ during the measurements. (Constancy of temperature to this amount is necessary even for approximate measurements.) The actual resistance measured in such an

apparatus as this will of course depend, not only on the conductivity of the solution, but also on the shape and size of the electrodes, their distance apart, etc. Since it is not practicable to make directly an accurate measurement of these, it is more convenient to calibrate the apparatus by means of a solution of known conductivity. For this purpose a $\frac{1}{50}$ normal potassium chloride solution is prepared, and its resistance is measured at some definite temperature. The ratio between this resistance and the known specific resistance of the solution gives the *resistance capacity* of the electrodes.

As mentioned above, the conductivity of the electrolyte varies with the concentration of the solution. The concentration is expressed in gram equivalents per cc. and is denoted by η . The dilution is the reciprocal of the concentration, *i.e.*, $\frac{1}{\eta}$ or ϕ , or the number of cc. in which 1 gram equivalent is dissolved.

The Equivalent Conductivity is then expressed by $\Lambda = \frac{x}{\eta} = x\phi$, that is, the conductivity of a solution in a cell which has its plates 1 cm. apart and each plate of an area of ϕ sq. cms. If the electrolyte is only partly dissociated, it is obvious that this value will increase with the dilution.

If now w equals the resistance measured in the apparatus for this $\frac{N}{50}$ KCl solution, the specific

conductivity x of which is

$$0.002397 \text{ at } 18^{\circ},$$

and

$$0.002768 \text{ at } 25^{\circ},$$

then

$$x = \frac{c}{w}, \text{ or } c = xw.$$

The value c denotes the resistance capacity of the particular arrangement of electrodes used, and is employed in all subsequent measurements of the conductivity. Having carefully determined the resistance capacity of the cell, make up a decinormal solution of oxalic and of citric acid, and determine their specific and equivalent conductivities, as also by dilution of a measured amount, those of $1/100$ and $1/1000$ normal solutions. In

these determinations $x = \frac{c}{w}$, where x = the specific conductivity of the solution, w = the resistance in ohms measured, and c = the resistance capacity of the cell.

Degree of Dissociation. The equivalent conductivity was defined above as the specific conductivity multiplied by the dilution, or the number of cc. which contain 1 gram equivalent of the solute. The value for the equivalent conductivity will increase with the dilution through increasing dissociation until it attains a limiting value, when the solute is completely dissociated. At this stage, the equivalent conductivity, which is denoted by Λ_{∞} is equal to the sum of two independent values for anion and cation. Thus $\Lambda_{\infty} = l_a + l_c$, where these values denote the relative rates of migration of the anion and cation. At any other dilution, the equivalent conductivity can be expressed by

$\Lambda v = \gamma (l_a + l_c)$, where γ equals the proportion of the solute which is dissociated. From this it follows that $\gamma = \frac{\Lambda v}{\Lambda_\infty}$. So that, to calculate the degree of dissociation of a substance at any dilution, we have simply to divide its equivalent conductivity at that dilution by the value given at infinite dilution, or when all is dissociated.

In the case of strong acids, bases and of salts, complete dissociation takes place at moderately high dilutions, but with weak acids and bases, the degree of dilution necessary to cause a complete breaking down into ions is too high to permit any accurate measurement being made of the conductivity, so that in these cases the value of Λ_∞ has to be derived indirectly. For this purpose use is made of the equation $\Lambda_\infty = l_a + l_c$, in which the value of the equivalent conductivity can be expressed as the sum of two separate values for anion and cation. In the case of a weak acid a measurement of Λ_∞ is made of the sodium salt, which is always completely dissociated at moderately high dilutions. By now subtracting from this found value of Λ_∞ , the known value for (l_{Na}), and adding the value for hydrogen (l_H), we obtain the value of Λ_∞ for the acid. The values for the equivalent conductivities of the H^+ and Na^+ ions, expressed in reciprocal ohms, at 18° , are as follows:—

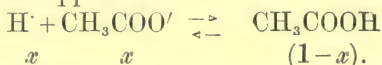
$$H^+ = 329.8$$

$$Na^+ = 43.55.$$

Similarly, with a weak base, this can be combined

with a strong acid and the difference between the value for OH' and the anion of the acid added to the value found for the equivalent conductivity of the salt.

Ostwald Dilution Law. Taking, as an example, the case of acetic acid, the following dissociation equilibrium applies:—



where x denotes the fraction of the acid which is broken down into ions.

If C is the concentration of the undissociated part and C_1 that of the ions, then according to the law of mass action, the following equation applies:

$$\frac{C_1^2}{C} = K \quad \text{where } K \text{ denotes the dissociation constant.}$$

If ϕ denotes the volume in cc. in which 1 gram equivalent of the substance is dissolved, then

$$C_1 = \frac{x}{\phi} \text{ and } C = \frac{1-x}{\phi}$$

$$\text{So that } K = \frac{x^2}{\phi(1-x)}$$

$$\text{Since } x = \frac{\Lambda v}{\Lambda_\infty}$$

$$\text{therefore } K = \frac{\Lambda^2 v}{\phi(\Lambda_\infty - \Lambda v)\Lambda_\infty}$$

The value K is an important constant which is a measure of the strength or affinity of acids and bases.

This should be calculated in the cases of the acids used in these experiments.

14. MEASUREMENT OF ELECTRO-MOTIVE FORCES AND SINGLE POTENTIAL DIFFERENCES BY USE OF THE COMPENSATION METHOD AND LIPPMANN ELECTROMETER.

General. The method employed is the Du-Bois Reymond's compensation method, and consists in compensating the E.M.F. of the cell (or combination of electrodes forming a cell) under examination by a known electro-motive force, capable of being adjusted for the particular case (compare Schuster and Lees, "Exercises in Practical Physics," p. 323). The attainment of compensation can be easily recognised by the use of a delicate galvanometer, or better, of a Lippmann electrometer. The diagram (Fig. 18) explains the principle of the method. A constant element (for example an accumulator) E , whose E.M.F. is greater than that of the cell to be measured, is connected to the ends of a resistance wire ab . The potential will fall uniformly from a to b ; hence, by making contact at the end b , and at the point c by means of the slider, we can take off any desired fraction of the E.M.F. of the cell E . The element A whose E.M.F. is to be measured is connected up in series with the capillary electrometer M to the end of the wire b , and with the movable contact c , which can slide along the wire and make contact at any point along it. Care is of course taken that the poles of

the cell are so joined to the circuit that the E.M.F. opposes that of the accumulator E; in this way we find a certain point at which the two opposing E.M.F.'s are in equilibrium and the value bc gives us the resistance of the wire, the fall of potential in which corresponds to the E.M.F. of

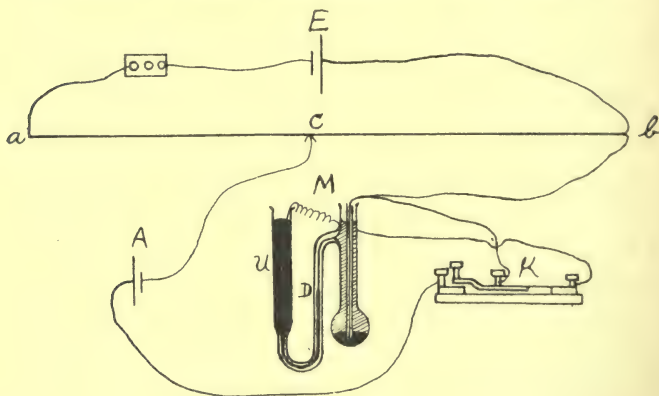


Fig. 18.

the cell. Similarly, repeating the determination with a standard cell in place of A (*e.g.*, a Clark or Weston cell), we have another value bc' . Now these resistances are in the same proportion to one another as the E.M.F.'s of the cells. Calling π the E.M.F. of the cell A and π' that of the standard cell, $\pi : \pi' = bc : bc' \therefore \pi = \pi' \frac{bc}{bc'}$.

The E.M.F. of the Clark cell at 15° is $1.4292 - 0.0012(t - 18^\circ)$, and the Weston cell $1.0187 - 0.000035(t - 18^\circ)$.

The Capillary Electrometer. The advantage of this electrometer consists in the action being practically a static one, no current being taken from the element to operate it. It is also very sensitive and will indicate as little as 0.0001 volt. The action of the electrometer depends upon the fact that the surface tension at the surface of separation of mercury and an electrolyte (in this case dilute sulphuric acid) is a function of the difference of potential existing at this surface. Now mercury, when in contact with sulphuric acid, acquires a positive charge through the separation on its surface of mercury ions, derived from traces of dissolved mercury which are always present. Any increase or decrease of this charge brought about by an outside source, alters the concentration of these ions in the immediate vicinity of the mercury, by causing some mercury either to pass into solution or else to be deposited on the surface. The effect of this change of concentration is to alter the potential between the mercury and the electrolyte; this affects the surface tension, and causes the thread to rise or fall in the capillary tube. In the above form of electrometer, this change of potential is mainly concentrated at the capillary column, as the larger surface of the mercury in the bulb renders this electrode practically unpolarisable. The height of the column of mercury in U above that in the capillary at D being determined by the surface tension at D, it follows that any change in the potential difference will cause the level at D to be raised or

lowered according as the mercury is made more positive or negative. There are several conditions to be observed to secure a proper working of the electrometer. Firstly, in order to compensate for slight differences of potential between the two mercury surfaces, which may be present before the measurement is made, it is necessary that the two surfaces be brought to the same potential immediately before the instrument is used. This is effected by having them permanently connected through the tapping key K, except for the moment during which the tap upon the key places the instrument in series with the cell circuit; the second condition is that the mercury in the capillary tube shall only be polarised as cathode, but even in this case the polarisation should not exceed one volt, or else hydrogen bubbles will be formed upon the surface. Polarisation as anode causes the mercury to become oxidised and so contaminated. To overcome either of the latter defects if they have occurred by accident, it is necessary to renew the surface of the mercury in the capillary by blowing until a drop has passed over into the larger vessel.

A modification of the Lippmann electrometer is seen in the apparatus in Fig. 19. This form of electrometer does not require the use of a lens for reading the thread. The mercury in the capillary at D is balanced by the column at H. The sensitiveness of the electrometer can be adjusted by altering the inclination of this capillary tube. The terminals are attached to *a* and *b*, and the

surface of mercury in the capillary can be renewed by allowing some of the mercury to run over from H into K. This column at H can, at any time, be replenished from K by inverting and causing some of the mercury to run round. Care must be taken on making measurements that the terminals

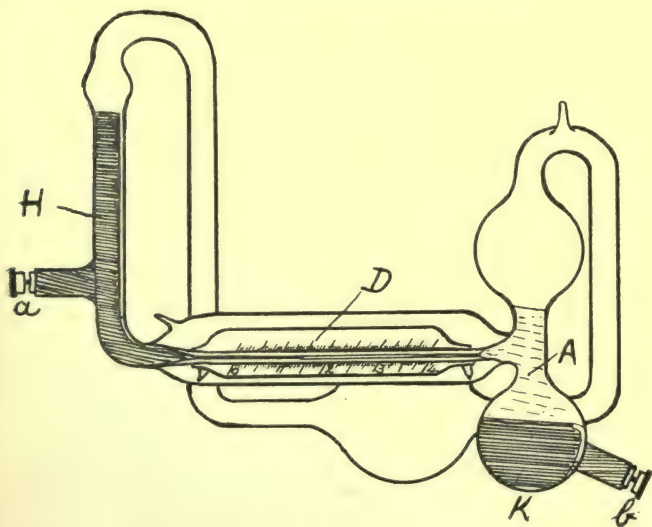


Fig. 19.

a and *b* are always in contact with the mercury H and K, and that there is a continuous column of dilute sulphuric acid between the mercury at D and at K.

Practical. As an example of the use of this method, the E.M.F. of a Daniell cell may be

determined and the single potential differences at the copper and zinc electrodes measured for the different dilutions of normal and tenth normal solutions.

The following solutions will be required:— 100 cc. normal copper sulphate should be prepared by weighing out 12.391 grams $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and making up to 100 cc. with water in a graduated flask. Similarly 100 cc. normal zinc sulphate by weighing out 14.269 grams $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$. Prepare a zinc rod and, after soldering a copper wire to one end, clean it with sandpaper and wash finally in a little dilute sulphuric acid. Similarly prepare a thick copper wire or thin narrow strip of sheet copper with wire attached; this should be coated with a film of electrolytic copper just before use and then washed in water.

Preparation of the "Normal Electrode." An electrode, the exact potential of which is known, is taken as a standard; with this we can construct experimental cells for the determination of the E.M.F. of the electrode with which it is joined. The mercury calomel electrode is prepared as follows: A wide mouth bottle (Fig. 20a) of about 50—100 cc. capacity is furnished with a rubber two-hole stopper. Through this stopper pass two tubes, one, into which a short platinum wire is sealed (A), reaching to the bottom, the other B, a short piece of narrow tubing bent at a right angle and reaching to just below the stopper. Sufficient pure mercury is poured into the clean bottle to just cover the bottom; the tube with platinum wire is adjusted so

that the platinum is covered by the mercury. A small quantity of calomel is added and then the bottle filled up with normal potassium chloride solution. A rubber tube provided with a pinch cock C and a piece of glass tubing twice bent, to serve as a dipping connection with the vessel containing the other electrode, is connected to the

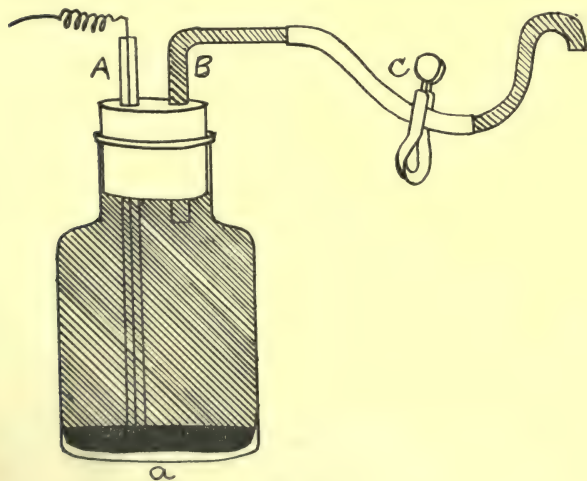


Fig. 20a.

apparatus, and the tubes are filled up with normal potassium chloride solution.

The single potential difference of the Normal Electrode is -0.560 volt at 18° and -0.564 at 25° .

If $\frac{1}{10}$ N. potassium chloride is used as the

[electrolyte the cell gives -0.612 volt at 18° , and -0.618 at 25° . That is, in the former case at 18° there is a tendency of 0.560 volt for the current to pass from the solution to the metal. This may be expressed graphically

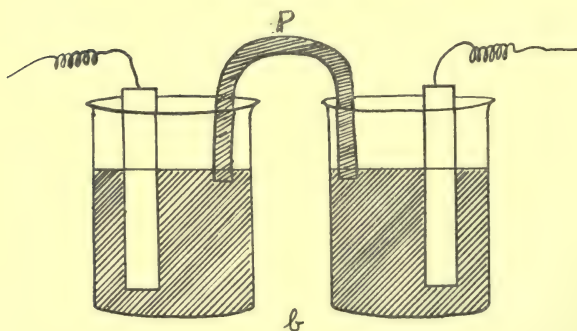
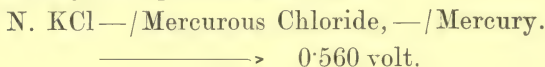


Fig. 20b.

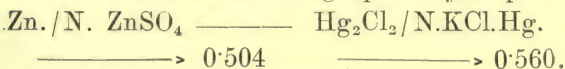
Although these values are only given to millivolts, the cell has been defined, and can be used with an accuracy of 0.1 millivolt.

The E.M.F. of a cell may, in most cases, be considered as the algebraic sum of the potential differences at the two poles. Taking the case of the Daniell cell, which we can construct as follows for studying its E.M.F.:—

Take a small glass vessel (Fig. 20b). Fill with normal copper sulphate, and insert a copper pole

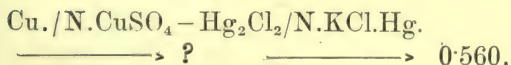
prepared as described above, and in a second vessel, containing normal zinc sulphate solution, place a zinc pole. The two solutions are joined together, just before measuring, by a piece of filter paper P, moistened with either solution (as soon as the measurement is complete the filter paper is removed). The combination so arranged is connected up with the bridge and electrometer, as explained above, and the E.M.F. measured and noted. The cell is then taken apart and the single potential differences measured by constructing cells with the normal electrode. The E.M.F.'s so found, together with a knowledge of the direction and value of the E.M.F. of the Normal Electrode, at once give us the E.M.F. Zinc/Zinc Sulphate and Copper/Copper Sulphate.

The values are best graphically represented



E.M.F. of combination

1.064



E.M.F. of combination

————— ?

The direction of the current within the cell is expressed by an arrow, and the value of its E.M.F. given by the number alongside. Thus, by subtraction from, or addition to, the values of the normal electrode already known, we obtain the

value and direction of the P.D. which is being measured.

Compare the value of the single P.D.s thus obtained with those previously measured for the complete Daniell cell.

Similar measurements must be made after diluting to $\frac{N}{10}$ CuSO_4 and $\frac{N}{10}$ ZnSO_4 . Finally, obtain some idea of the sensitiveness of the electrometer by moving the slider short distances (1 to 2 mm.) on each side of the zero point and noting the change of position of the mercury meniscus.

[NOTE.] The potential difference which arises between a metal and a salt solution when in contact may be expressed by a formula which has been derived by Nernst by considering the change in free energy. The view is taken that every metal, in contact with a liquid, possesses a certain definite solution pressure whereby the metal tends to pass into solution in the form of ions. As these ions carry a positive charge, the metal electrode must receive a corresponding negative charge. An electrical double layer is thus formed, the negatively charged metal attracting the positively charged ions, so that a state of equilibrium is finally reached when the electro-static attraction in the double layer just balances the solution pressure of the metal. If ions of the metal are already present in the solution, they will, by virtue of their osmotic pressure, oppose the solution tendency of the metal, so that, in this case, the P.D. set up between the metal and the electrolyte will just equal the difference between the solution pressure of the metal and the osmotic pressure of the ions. If the osmotic pressure of the ions exceeds the solution pressure of the metal, then ions will be deposited on the electrode imparting to it a positive charge. The amount of this charge can be calculated by considering the work which

is involved when a metal of solution pressure P passes into ions of osmotic pressure p_1 . The passage of the metal into ions of osmotic pressure P (where P equals the solution pressure of the metal) takes place without any change in energy, since the change takes place reversibly and spontaneously. The work effected by the ions changing from the osmotic pressure P to p_1 is entirely analogous to the case of a gas.

If we represent the change of pressure as taking place in an infinite number of intermediate stages, then during each one we have the work $w = v dp$, where v is the volume, and dp the infinitely small change of pressure during the particular stage. The sum of all these separate stages gives us the total work, thus $W = \int_{p_1}^P v dp$, where p changes continuously from P to p_1 .

Since $v = \frac{RT}{p}$, then

$$W = RT \int_{p_1}^P \frac{dp}{p} = RT \ln \frac{P}{p_1}.$$

where \ln denotes natural logarithms.

Now the work may be expressed electrically by putting $W = eb$, where e corresponds to the voltage or potential which is obtained in this change, and b the quantity of electricity which is associated with 1 gram atom of metal when it passes into the ionic state. Hence $eb = RT \ln \frac{P}{p_1}$. If now, e is measured in volts, then $b = nF$ where n is the valency of the metal, and F denotes the electro-chemical equivalent (96540 coulombs). Placing for R its value in calories (1.99) and dividing by .239 (since 1 volt coulomb = .239 cal.), we have $R = 8.316$, expressed in electrical units. The natural logarithms are reduced by ordinary logarithms by dividing by 0.4343, and we have $e = \frac{8.316T}{.4343n.96540} \log \frac{P}{p_1}$ volt.

(In the case of a monovalent substance, and at the temperature 18° (291° abs.), this formula takes the value $0.058 \log \frac{P}{P_1}$).

The above formula has also important applications in dealing with concentration cells, polarisation effects, etc.

15. GAS CELLS.

We have seen above (p. 90) how the solution of a metal can act electromotively and cause the generation of an electric current. This is due to the metal possessing a "solution pressure," or tendency to ionise which sets up a definite P.D. between the metal and the electrolyte.

Gases are able to act in the same manner when in presence of an unattackable electrode in which they have the power of dissolving. For instance, hydrogen when present in solution in such an electrode will tend to ionise thus $H_2 \rightarrow 2H^+$, and leave a negative charge on the electrode. The E.M.F of such an electrode will depend on the pressure of free hydrogen in the space above, since there is a constant ratio between this and the amount in the electrode. The potential difference can be expressed by a formula similar to that used for the potentials of the metals, viz.,

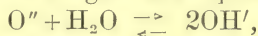
$$e = \frac{0.0002T}{2} \log \frac{k_1[H_2]}{[H]^2}$$

where k_1 is a constant representing the solution pressure of the hydrogen, and $[H_2]$ is the concentration of the hydrogen in the electrode, and $[H]$ that of the hydrogen ions in solution.

[NOTE.] Taking for T the ordinary room temperature 18° , we have $-e = \frac{0.058}{2} \log \frac{k_1[H_2]}{[H]^2}$

From this formula it follows that if a denotes the E.M.F. when the pressure of the hydrogen above the electrode is 1 atmosphere, and the solution normal with respect to hydrogen ions, then at any other concentration the E.M.F. will be given by $e = a - \frac{0.058}{2} \log \frac{[H_2]}{[H]^2} = a - 0.029 \log [H_2] + 0.058 \log [H]$.

In the same way gases which form anions will act electromotively, such as chlorine and oxygen. In the case of the latter we have the following reaction:— $O_2 \rightarrow 2O'' + 4\oplus$. The O'' ion then reacts with water to give the equilibrium



so that $[O''] = K[OH']^2$.

The E.M.F. of the oxygen electrode is therefore expressed by

$$e' = \frac{0.0002T}{4} \log \frac{k'[O_2]}{[O'']^2} = \frac{0.0002T}{4} \log \frac{k_0[O_2]}{[OH']^4}$$

where $k_0 = \frac{k'}{K}$

[NOTE.] In this case, if b denotes the E.M.F. of the electrode when the pressure of oxygen is atmospheric, and the solution normal with regard to OH ions, then the E.M.F. at any other concentration is given by $e = b + \frac{0.058}{4} \log \frac{[O_2]}{[OH']^4}$

If two gas electrodes, such as those with hydrogen and oxygen, are combined by connecting the electrolyte in each, we have an arrangement in which these gases combine isothermally at ordinary temperatures with the production of

electric energy. This electromotive action will continue, yielding a current, as long as any gas remains about both electrodes. It is important, for this purpose, that the platinum electrodes should be well platinised in order to enable the solution of the gases. The electromotive force of this combination of a hydrogen and oxygen electrode is given by the formula—

$$e = +e' - (-e'') = e' + e''$$

$$\begin{aligned} e &= \frac{0.0002T}{2} \log \frac{k_1[H_2]}{[H\cdot]^2} + \frac{0.0002T}{4} \log \frac{k_0[O_2]}{[OH']^4} \\ &= \frac{0.0002T}{2} (\log k_1[H_2](k_0[O_2])^{\frac{1}{2}} - 2 \log [H\cdot] [OH']) \end{aligned}$$

Now if both electrodes are immersed in the same electrolyte, then $[H\cdot][OH'] = K$, since, according to the law of mass action, the product of hydroxyl and of hydrogen ions must always be a constant

$$\therefore e = 0.0001T \log k_2[H_2][O_2]^{\frac{1}{2}} \text{ where } k_2 = \frac{k_1 k_0^{\frac{1}{2}}}{K^2}$$

From this we see that the E.M.F. of an oxygen-hydrogen cell is independent of the nature of the electrolyte, providing the same solution is around both electrodes, and such is indeed found to be the case in practice.

As a rule the potentials of gas electrodes do not quite reach their maximum value until after standing for some time, in some cases, a lapse of several days being necessary.

As the E.M.F. of a gas electrode varies directly as the logarithm of the amount of gas present, considerable differences of pressure and amounts of

impurities only cause a small alteration in the potential.

Practical. The vessels to be used as oxygen and hydrogen electrodes have the form shown in Fig. 21. The glass cylinder A is coated with a layer of platinum and serves as an electrode.*

A thin piece of platinum wire is sealed through the bottom of this glass tube so as to make connection between the outside coating and mercury which is placed inside. This mercury enables connection to be made with the leading in wire.

The electrolyte is placed inside the vessel to the level B so as to partly cover the foil, and a slow current of the gas (hydrogen or oxygen) is allowed to pass through, entering at C, bubbling through the electrolyte, and passing out through the wash bottle at D.

A syphon tube is inserted in the cup E, and serves to make connection with the electrolyte of another element. This element can then be combined with a second, *e.g.*, a hydrogen one with an oxygen electrode, or either with a calomel electrode. This is arranged by immersing the syphon tubes from each vessel into any common

* Glass can be conveniently covered with an adherent film of platinum by coating with a solution prepared as described below, and then warming to about 200° , when decomposition takes place.

0.3 gm. platinic chloride is moistened with conc. HCl and mixed with 1 cc. conc. boric acid solution. After dissolving in alcohol, 1 cc. French turpentine and 2 cc. oil of lavender are added.

electrolyte, so as to form a connection, through the solution, between the two electrodes.

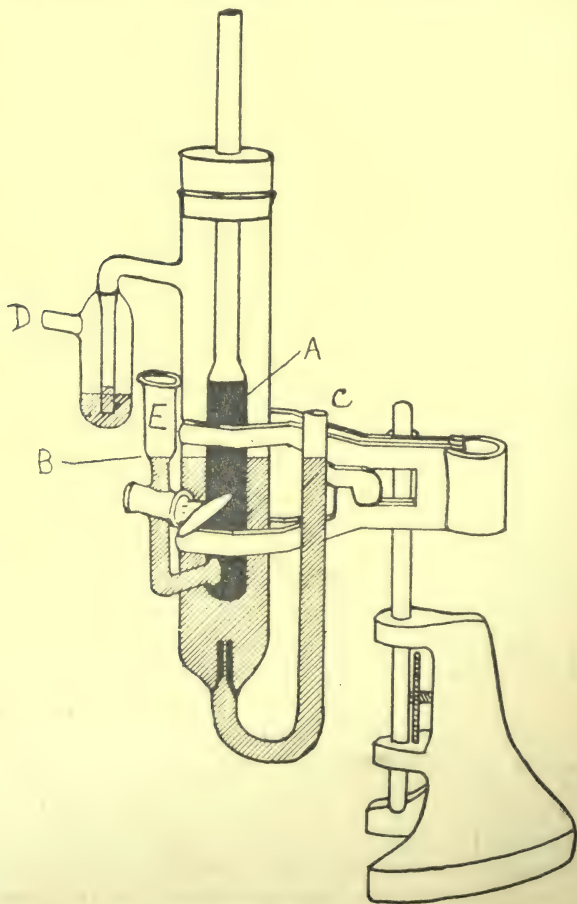


Fig. 21.

The E.M.F. of such a combination can then be measured by leading wires from the two electrodes to a suitable potentiometer or slide wire bridge where the potential can be balanced by that of a known amount. (Compare p. 82.)

These platinum coated glass cylinders sometimes give untrustworthy results, probably on account of the influence of some impurity introduced in the platinum. More reliable results are usually obtained by using rectangular electrodes of thin platinum foil. A lapse of several hours is, however, sometimes needed in this case for the platinum to become saturated with the gas and give the maximum value.

An electrode, such as the above, in which hydrogen at atmospheric pressure, in contact with platinum, is placed over a solution of acid of normal strength is sometimes taken as a standard of single potential difference. The E.M.F. is +0.277 volt.

16. DECOMPOSITION VOLTAGES.

In order to cause the electrolytic decomposition of a solution it is, in every case, necessary to apply a certain minimum E.M.F. below which continuous electrolysis will not take place. The process may be regarded as analogous to that of the boiling of a liquid, where there is a definite temperature at which continuous vaporisation takes place, under any given pressure. Below this temperature a quantity of vapour is evolved until

present in the surrounding atmosphere at a certain pressure, when further action ceases. An exactly similar phenomenon takes place in the electrolysis of a liquid. Here the smallest E.M.F. causes a certain momentary decomposition, which almost entirely ceases as soon as the products of the electrolysis have attained a certain concentration on the electrodes. The presence of these separated elements on the electrodes then sets up an opposing E.M.F. which just balances that applied. If these products are gases they will slowly be removed by dissolving in the solution and diffusing away, so that a small residual current will be maintained to restore this loss. When the products of an electrolysis are gases, the action further follows the analogy of the boiling of a liquid in that the decomposition point is a function of the atmospheric pressure, and at very low pressure takes place with an expenditure of energy which becomes zero or even negative.*

The reactions at the electrodes during electrolysis are of a completely reversible nature, the

* This particular case of the effect of pressure on the decomposition voltage of water is a good illustration of the discrepancy which exists between the *total* and *free* energy of a chemical action.

We are here considering the free energy or maximum work which can be yielded by the reaction, and this quantity varies with the concentration of the reacting substances and becomes zero when these are in equilibrium with the product. The total energy, on the other hand, which is equivalent to the calorific value of the reaction is always constant at any given temperature.

same E.M.F. being necessary to decompose a liquid as that which is given in a cell where the constituents combine electromotively to form that compound. As in a primary cell, so in the decomposition of a solution, we are always dealing with two additive effects, the reaction at the anode and that at the cathode, so that the decomposition voltage of a liquid is equal to the sum of the single values for anion and cation. The potential difference at the two electrodes during electrolysis, can be separately measured by the use of a Normal Electrode arranged as shown in the diagram (Fig. 22).

A and B are connected to a source of current at sufficient potential just to cause continuous electrolysis. The syphon tube of the normal element or hydrogen electrode N is immersed in the solution, and care must be taken that the electrolyte fills this tube and connects the solutions of both cells. The syphon tube S should be placed outside the line of flow of the current between the electrodes A and B.

The single potential difference between B and the solution can, with the above arrangement, be measured as in the case of the potentials between metals and salt solutions, which is described on p. 88. The E.M.F. between B and N is measured by the compensation method, with the use of the Lippmann electrometer. By subtracting from this the known value for the E.M.F. of the normal electrode, we obtain the potential difference between B and the solution. Similarly, that

between A and the solution is measured by joining A and N to the potentiometer.

[NOTE.] The formula which was deduced for the single potential difference between a metal and a salt solution also applies to the voltage necessary for decomposition, i.e.,

$$e = RT \ln. \frac{P}{p}$$

Here P represents the solution pressure of the separated element and p the osmotic pressure of the ions in solution. This formula thus applies to the reversible process of the decomposition of a solution and of its electro-chemical synthesis. It must be remembered that solutions usually contain a good many different kinds of ions which exist in very varying quantities, and that in using the above formula, each of these varieties of ions must be treated separately as they all possess different decomposition potentials. Thus, in the case of pure water, we have the ions H' , OH' and O'' , and in a solution of H_2SO_4 there occur, in addition, HSO_4' and SO_4'' .

The decomposition point of the different ions was investigated by Nernst and Glaser (*Zeit. Elektroch.*, iv, 355, 373, 397, [1898]). Two electrodes were taken, one of a large platinum foil and the other of a short wire or fine point of the same metal. The electrodes were joined in series with a delicate galvanometer, and the applied voltage gradually increased, until a sudden rise in the galvanometer reading occurred, indicating that the separation point of some ion on the point electrode had been reached.

By making the platinum point cathode, and the foil anode, and saturating the latter with oxygen, the voltage at which continuous decomposition set in gave the difference between the decomposition potential of the cation and the known value for that of the oxygen electrode. To investigate the separation of an anion, the point was used as anode and the foil made into a hydrogen electrode.

With an ion which is present in large quantities, a sharp rise was obtained in the curve, which gives the relation between

P.D. and current, as soon as the decomposition value was reached, while, if present only in small quantities, a smaller rise, or simply a bend in the curve resulted. In this way values for the separation potentials were found as follow.

Measured against the hydrogen electrode as zero, the values were :—

For O"	1.08 volt
OH'	1.67 "
SO ₄ "	1.98 "
HSO ₄ "	2.65 "

For cations, measured against the oxygen electrode as zero (whereby H⁺ separates at 1.08),

K ⁺	at 1.3
Na ⁺	at 1.28
Ba ⁺	at 1.18
Mg ⁺	at 1.39

In the reversible reaction in an oxyhydrogen cell, we only deal with the H⁺ and O²⁻ ions, the combined potential of which is 1.08 volt (at N.T.P.). In the electrolysis of water, however, on account of the very small quantity of the O²⁻ ions present, the decomposition at 1.1 volt is almost imperceptible, and with platinum electrodes it is only at 1.68 volt, when the OH' ion separates (on platinum) that any considerable decomposition sets in. The difference between this theoretical point, 1.08 volt, and the actual voltage necessary for the decomposition of water, 1.68 volt has also been ascribed to the overvoltage effect in oxygen evolution on platinum (cf. *infra*).

Overvoltage. In certain cases in practical electrolysis, where gases are the products of decomposition, a discrepancy appears between the theoretical decomposition potential and the voltage actually necessary for the decomposition of the solution. When platinum electrodes, with well platinised surface are used, decomposition at the

cathode takes place at almost exactly the theoretical value, but with electrodes of other metals a higher E.M.F. is usually necessary. This effect, which was first investigated by Caspari,* is known as overvoltage, and is of far-reaching importance in technical electrolyses.

Caspari took cathodes of different metals, mostly in the form of short thin wires, and, while gradually increasing the voltage, noticed the point at which the formation of bubbles of hydrogen first took place. The value for the single potential difference was then compared with that given by the reversible oxyhydrogen cell and the difference was termed the overvoltage. With an electrolyte of normal sulphuric acid, the cathodic overvoltage was found, in the case of platinised platinum, to be as low as 0.005 volt, and with smooth platinum, 0.09 volt. The value was relatively low with all the noble metals and with iron and nickel, but increased with the more electro-positive metals: cadmium, tin, lead, zinc, and mercury, amounting, in the lead case, to as much as 0.78 volt.

The overvoltage varies somewhat with the nature of the surface of the metal being usually a little higher with a smooth than with a rough surface of metal.

In the case of the above metals the high overvoltages are probably in part connected with the fact that before hydrogen can be liberated on their surface the high solution pressure of the metal

* *Zeit. Phys. Chem.*, xxx, 89, 1899.

must be first overcome. This view also provides an explanation of the fact that in the case of those metals which show a high overvoltage, the presence of traces of impurities causes a large lowering of the overvoltage. In such cases, the presence of substances with lower solution pressures enables the evolution of hydrogen locally. In the case of zinc, with an amalgamated surface, the presence of the layer of mercury prevents the impurities present from lowering the overvoltage by always presenting a surface film of mercury, so that zinc, treated in this way, is not dissolved by acids.

Overvoltage at the Anode. The potential at which continuous electrolysis of water takes place was found, in the case where platinum electrodes were used, to be 1.68 volt. The decomposition point with electrodes of other metals was investigated by Coehn and Osaka,* who used a solution of potassium hydroxide and found that the following P.D.s between anode and cathode were necessary to cause continuous electrolysis:—

With spongy nickel	1.28
„ smooth nickel	1.35
„ cobalt	1.36
„ iron...	1.47
„ platinised platinum	1.47
„ smooth palladium	1.65
„ smooth platinum	1.67
„ gold	1.75

* *Zeit. anorg. Chem.*, xxxiv, 86, 1903.

The very small residual current below these voltages showed an increase at 1.1 volt, showing this to be the real decomposition point of water. Anodic polarisation increases with time, at first rapidly, then gradually converging to a maximum value at which it remains constant. The same effect is observed in a smaller degree in the liberation of hydrogen on cathodes of smooth metals, when a rather high current density is used. The phenomenon of overvoltage is a very important factor in reactions in which oxidations or reductions are effected electrolytically. As explained on p. 106, chemical oxidations and reductions consist in the taking up of positive and negative charges of electricity respectively. The potential at which these charges must be applied varies with different substances, and the more difficult it is to oxidise or reduce a substance the higher the potential must be. The liberation of the ions in solution sets a practical limit to the potential difference which can be maintained between the electrode and the electrolyte. By selecting for the electrode a metal which shows a high overvoltage, this potential difference can be raised, and oxidations or reductions effected which would not be possible with the lower value. The voltage between electrode and electrolyte can also be raised by increasing the current density. It is partly for this reason of securing definite potential differences that the current density has to be carefully regulated in conducting electrolytic reactions.

The part played by overvoltage in effecting oxidations or reductions can also be regarded as due to the pressure of the gas at the surface of the electrode.

Practical. By means of the apparatus shown in Fig. 22, measure the single potential differences

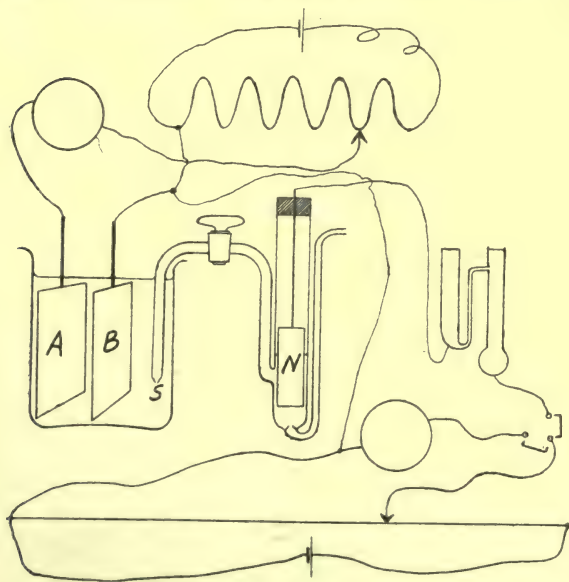


Fig. 22.

at the electrodes during the electrolysis of dilute sulphuric acid. Take first electrodes of platinised platinum, and by means of the regulating resistance shown in the figure gradually increase the voltage between the electrodes until a continuous electrolysis just sets in. Using either a calomel

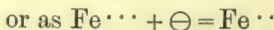
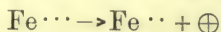
electrode or a hydrogen electrode, and by joining N, and either A, or B, to the potentiometer, the combined potential of the normal electrode and that at A or B is measured. From this the single potential difference between the electrolyte and either electrode can be calculated.

Substitute now for the platinum cathode one of the other metals, such as nickel, copper and lead, and find the magnitude of the overvoltage.

In the case of copper see what difference exists between samples of the metal when the surface has been freshly electro-deposited, when hardened, and when annealed.

17. ELECTRICAL POTENTIALS OF OXIDISING AND REDUCING MEDIA.

If an unattackable electrode, such as platinum, is placed in an oxidising solution it will acquire a positive charge relatively to the solution, and if placed in a reducing solution, it will receive a negative charge. A change from a higher to a lower stage of oxidation is always accompanied by the surrender of a positive, or else by the taking up of a negative charge. Thus, the change from the ferric ion to ferrous ion can be expressed as

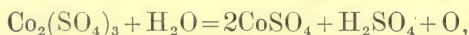


Reducing agents, on the other hand, change from a lower to a higher stage of oxidation by the surrender of a negative or else by taking up a positive charge.

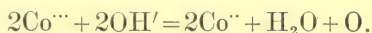
Thus $\text{Fe}^{\cdot\cdot} \rightarrow \text{Fe}^{\cdot\cdot\cdot} + \ominus$ or $\text{Fe}^{\cdot\cdot} + \oplus \rightarrow \text{Fe}^{\cdot\cdot\cdot}$

Similarly with zinc $\text{Zn} \rightarrow \text{Zn}^{\cdot} + \ominus$ and tin $\text{Sn}^{\cdot\cdot} \rightarrow \text{Sn}^{\cdot\cdot\cdot\cdot} + 2\ominus$.

If an oxidising substance is present in an aqueous solution, its affinity for a negative charge will tend to deprive the hydroxyl ions of their charge, and liberate oxygen in the free state. Thus, in the case of cobaltic sulphate, when in presence of sulphuric acid, this affinity is sufficient to cause the spontaneous evolution of oxygen, reaction taking place according to the equation:

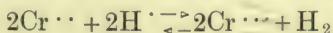
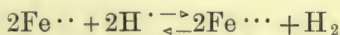


or expressed ionically:—



In presence of a normal solution of hydrochloric acid, chlorine is liberated. Similarly, a reducing body will tend to liberate the hydrogen by depriving the ions of their positive charge.

In cases where these oxidation and reduction tendencies are not sufficient to decompose water at ordinary pressures, a certain amount of hydrogen or oxygen will, in every case, be liberated until it reaches a certain pressure in the solution and satisfies an equilibrium as expressed by the equation—



The potential set up on the electrode by any of these solutions can be calculated indirectly from

the effect of this hydrogen or oxygen in the following manner:—

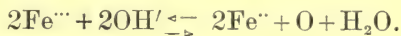
Taking the case of reducing media, a platinum plate, if immersed in such solutions, will dissolve a definite amount of hydrogen. As we have seen in the chapter on gas cells, this dissolved hydrogen will exert an electrolytic solution pressure, causing it to become negatively charged, and the amount of this charge will depend on the quantity of free hydrogen in solution, and on the opposing osmotic pressure of the hydrogen ions. In this way the potential difference arising between a reducing solution and a platinum plate gives a quantitative value to the reduction tendency.

In the case of the ferrous ion (when in presence of some ferric), acting as represented in the above equation, the concentration of the hydrogen may, according to the law of mass action, be expressed as $H_2 = \frac{k_1(Fe^{..})^2(H\cdot)^2}{(Fe^{...})^2}$

The hydrogen will then act electromotively, thus, $H_2 \rightarrow 2H\cdot + 2\ominus$, and will give an E.M.F. which can be denoted by $\frac{0\cdot0002T}{2} \log \frac{k_2 H_2}{(H\cdot)^2}$ which equals $\frac{0\cdot0002T}{2} \log \frac{k'(Fe^{..})^2(H\cdot)^2}{(H\cdot)^2(Fe^{...})^2} = 0\cdot0002T \log \frac{k'Fe^{..}}{Fe^{...}}$ (..... α) where $k' = k_1 k_2$.

A mixture of a ferrous and ferric salt may also be regarded as an oxidising medium and can be

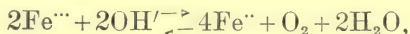
dealt with in an analogous manner from the standpoint of the following equation:—



This equilibrium must exist simultaneously with the former $2\text{Fe}^{\cdots} + 2\text{H}' \rightleftharpoons 2\text{Fe}^{\cdots} + \text{H}_2$.

In these systems the H' and OH' must also be in equilibrium, viz., $\text{H}' \times \text{OH}' = k.\text{H}_2\text{O}$.

Representing now the oxidising tendency of this salt by the equation—



then, according to the law of mass action,

$$\text{O}_2 = \frac{k_3(\text{Fe}^{\cdots})^4 (\text{OH}')^4}{(\text{Fe}^{\cdots})^4}.$$

The oxygen potential is then expressed by the equation—

$$\begin{aligned} -e &= \frac{0.0002T}{4} \log \frac{k(\text{O}_2)}{(\text{OH}')^4} \\ &= \frac{0.0002T}{4} \log \frac{(k'')^4 (\text{Fe}^{\cdots})^4 (\text{OH}')^4}{(\text{Fe}^{\cdots})^4 ((\text{OH}')^4)} \\ &= 0.0002T \log k'' \frac{(\text{Fe}^{\cdots})}{(\text{Fe}^{\cdots})} (\dots\dots\dots\beta) \end{aligned}$$

where $k_3 k_4 = (k'')^4$.

These formulæ can be derived directly by representing the change of ferrous to the ferric ion as $\text{Fe}^{\cdots} \rightarrow \text{Fe}^{\cdots} + \ominus$. In this reaction the ferrous ion is regarded as having a certain tendency to take on an additional positive charge, which is analogous to the solution pressure of a metal

(*vide* p. 90), and consequently the E.M.F. may be expressed by the formula

$$+e = 0.0002T \log \frac{k'(\text{Fe}^{\cdot\cdot})}{(\text{Fe}^{\cdot\cdot\cdot})}$$

which is the same as α .

The reduction of ferric to ferrous may similarly be represented by $\text{Fe}^{\cdot\cdot\cdot} \rightarrow \text{Fe}^{\cdot\cdot} + \oplus$, and the E.M.F. expressed by the formula

$$-e = 0.0002T \log \frac{k''(\text{Fe}^{\cdot\cdot\cdot})}{(\text{Fe}^{\cdot\cdot})}$$

which is the same as β .

By taking $k' = \frac{1}{k''}$, we see that in the formulæ α and β , denoting the potentials of a ferric-ferrous mixture,—regarded in the one case as a reducing compound and in the other as an oxidising compound—are equal.

The extent to which one solution can oxidise or reduce another can readily be ascertained by measuring the oxidation or reduction potentials at various relative dilutions. For instance, in a solution containing a mixture of ferrous and ferric ions, the largest excess of the latter never gives a positive charge as high as the most dilute solution of gold chloride. Consequently gold is always precipitated from such a solution by a ferrous salt.

Further, a measurement of the effect of dilution on the potential of an oxidising or reducing process, will often give valuable evidence concerning the nature of a reaction and the number of molecules involved.

It will be observed, from the above formulæ, that oxidising agents are more powerful in acid, and reducing agents in alkaline solutions. This is on account of the higher E.M.F. set up, in the former case through the scarcity of the hydroxyl ions which makes the oxygen potential higher, and in the latter case through the small number of the hydrogen ions, which raises the potential of the dissolving hydrogen. Thus, in the case of ceric and cerous sulphates in acid and in alkaline solutions the following values have been found for the single potential differences between a platinum plate and the solutions:—

(a) $0\cdot1\text{Mol. Ce(SO}_4)_2 + 0\cdot05\text{Mol. Ce}_2(\text{SO}_4)_3 + 1\cdot0\text{Mol.}$

$\text{H}_2\text{SO}_4 = +1\cdot12\text{ volt.}$

(b) $0\cdot15\text{CeO}_2, 0\cdot05\text{Ce}_2\text{O}_3\text{ in conc. K}_2\text{CO}_3$

$= -0\cdot27\text{ volt.}$

It must be remembered that oxidation and reduction effects can only be regarded from a relative standpoint, just as in the case of the classification of metals in the electromotive series as positive or negative. The nature of the charge which a solution imparts to the immersed electrode will of course depend upon the definition of the zero potential.

Practical. The measurement of oxidation and reduction potentials is carried out in precisely the same manner as that used for the measurement of the single potential differences

between metals and salt solutions. A platinum electrode, with well platinised surface forms one terminal, and is immersed in the solution which it is desired to investigate. This electrode is then connected with a suitable normal electrode,—either a calomel or a hydrogen electrode, the liquids in each being joined by means of a syphon, either directly or through any intermediate electrolyte. The electrode of the normal element forms the second terminal, and thus completes the cell. This is joined to a Lippmann electrometer, through a tapping key, and on to a slide wire potentiometer, which is adjusted until the electrometer indicates that the E.M.F. of the cell is just compensated by that along the wire. If ac is the length of slide wire when this balance has been effected, and ac' is the position of balance when a standard cell (Weston or Clark) is used in place of the electrode combination, then the E.M.F. of the latter is equal to $E \frac{ac}{ac'}$ where E is the E.M.F. of the standard cell. On subtracting from E the value for the normal electrode e_n , we have e_1 , the single potential difference between the liquid and the platinum electrode.

It is to be noted that, in many cases, the charge on the electrode only reaches its maximum value after the lapse of a considerable time.

Measure the potential of the following oxidation media :—

0.5 Normal HClO in N.H ₂ SO ₄	+ 1.26 volt.
1.0 Normal HClO ₃	+ 1.05 „
6.0 Normal HClO ₃	+ 1.20 „
HNO ₃ (95%)	+ .82 „
HNO ₃ (35%)	+ .75 „
HNO ₃ (6%)	+ .67 „
0.1 Normal HMnO ₄	+ 1.18 „
0.09 Mol.FeCl ₃ + 0.01 Mol.FeCl ₂	+ .43 „
0.01 Mol.FeCl ₃ + 0.09 Mol.FeCl ₂	+ .32 „

These figures are based on the value 0.277 for the normal hydrogen electrode, and - .612 for the deci-normal calomel electrode.

Measure the potential of the following reducing media :—

- 1.0 N. Cu₂Cl₂ in concentrated HCl solution.
- 1.0 N. Cu₂Cl₂ in ammoniacal solution.
- 0.1 N. SnCl₂ in 5 N. HCL solution.
- 1.0 N. Na₂SnO₃ in 5 N. NaOH solution.

Measurement of the Oxidation Potentials of Peroxides. Cover a platinum foil electrode with a deposit of manganese peroxide or lead peroxide. This can be conveniently carried out by electro-deposition from a solution of a salt of the metal in presence of 10% nitric acid, when a coherent deposit of the peroxide forms on the anode (compare p. 60). These peroxides are good conductors of electricity. Measurements can now be made of the oxidation potentials of these electrodes in various electrolytes by immersing in the solution and

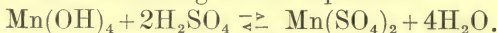
combining with a second normal electrode in the manner described above with the platinum foil.

The following cases should be investigated :—

Experi- ment.	Electrode.	Electrolyte.	Single Potential Difference.
1	PbO ₂	1.0 N. H ₂ SO ₄	—
2	PbO ₂	0.5 N. H ₂ SO ₄	—
3	MnO ₂	0.5 N. H ₂ SO ₄ + 0.05 N. MnSO ₄	—
4	MnO ₂	0.1 N. KOH	—

The mechanism of the reaction in the case of manganese peroxide in a sulphuric acid electrolyte is as follows :—

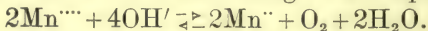
The solution in the neighbourhood of the electrode becomes saturated with Mn(OH)₄ which then reacts according to the equation—



Since the amount of Mn(OH)₄ and H₂O may be taken as constant, it follows that

$$\frac{[\text{H}_2\text{SO}_4]^2}{[\text{Mn(SO}_4)_2]} = k, \text{ or } \frac{[\text{H}']^4}{[\text{Mn}\cdots]} = k.$$

The Mn⁺⁺⁺ then reacts according to the equation—



The concentration of this free oxygen is expressed by the formula—

$$[\text{O}_2] = \frac{K[\text{Mn}\cdots]^2 [\text{OH}']^4}{[\text{Mn}^{\cdot\cdot}]^2},$$

Consequently, the oxidation potential is equal to

$$\begin{aligned} \frac{0.0002T}{4} \log \frac{k_1[\text{Mn}\cdots]^2 [\text{OH}']^4}{[\text{OH}']^4 [\text{Mn}^{\cdot\cdot}]^2} \\ = \frac{0.0002T}{2} \log \frac{k'[\text{Mn}\cdots]}{[\text{Mn}^{\cdot\cdot}]}, \end{aligned}$$

Since, as shown above, $[\text{Mn}\cdots] = \frac{[\text{H}\cdot]^4}{4k}$

$$\text{then } e = \frac{0.0002T}{2} \log \frac{k^2 [\text{H}\cdot]^4}{[\text{Mn}\cdots]},$$

From this, it is seen that the oxidation potential of MnO_2 is more positive the higher the concentration of acid, and conversely, in an alkaline solution, where the concentration of the $\text{H}\cdot$ is very low, is more negative. An exactly similar relation holds in the case of PbO_2 .

PART II.

ELECTROLYTIC PREPARATIONS.

1. ELECTRO-CHEMICAL METHODS OF REDUCTION.

Reduction of Aromatic Nitro Compounds. The final product in the reduction of aromatic nitro compounds is the amine, but a large number of compounds can be obtained from intermediate stages of reduction by varying the conditions of the electrolysis, such as the choice of electrolyte, electrodes, etc. Thus, in acid solutions, it has been found that when platinum electrodes are used, the amines are seldom formed in large amounts. Elbs* found that if a zinc cathode is substituted for one of platinum, the reduction of nitrobenzene can be carried through to aniline.

Later† it was found that an addition of zinc salt to the liquid filling the cathode portion of the cell led to essentially the same results, even when other metals are used as the cathode.

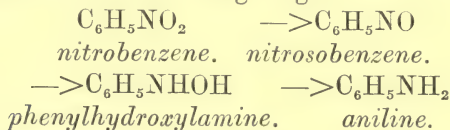
The reduction to aniline can also be brought about with a lead cathode.

* *Chem. Ztg.*, xvii, 209 (1893); *Zeit. Elektroch.*, ii, 472 (1896).

† Elbs and Silbermann. *Zeit. Elektroch.*, vii, 589 (1901).

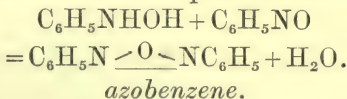
The influence of the nature of the metal forming the electrode is explained by the over-voltage effect during hydrogen evolution (see p. 101).

Taking the case of nitrobenzene, the reduction proceeds in the following stages:—

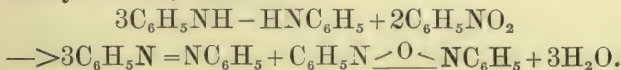


In moderately acid solutions, nitrobenzene can, by powerful reduction, be completely converted into aniline. If, however, the solution is very strongly acid, a portion of the intermediate product, phenylhydroxylamine, is transformed into the isomeric p. amidophenol, which cannot be further reduced. $\text{C}_6\text{H}_5\text{NHOH} = \text{C}_6\text{H}_4 \begin{smallmatrix} \nearrow \text{OH} \\ \searrow \text{NH}_2 \end{smallmatrix}$

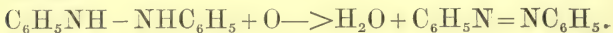
In alkaline solutions, the following reaction between the intermediate products takes place:—



This reaction takes place very quickly, and by using a nickel cathode, no further reduction of the phenylhydroxylamine to aniline occurs. The azobenzene, however, is reduced to hydrazobenzene, which then quickly reacts with the unchanged nitrobenzene to form azobenzene and azoxybenzene, thus—



In addition to this reaction, the hydrazobenzene is rapidly oxidised by the oxygen of the air to azobenzene.



By virtue of these reactions it is possible to obtain excellent yields of azobenzene under suitable conditions of working.

(a) PREPARATION OF ANILINE FROM NITROBENZENE.

A tall beaker is taken and a porous pot placed inside to serve as anode compartment, while the space between the porous pot and the walls of the beaker contains the cathode liquor. For the cathode liquor, 20 grams of nitrobenzene, and 120 cc. of hydrochloric acid (s.g. 1.19) are taken and mixed together so as to form an emulsion. This is placed in the beaker and the electrolysis carried out at the room temperature. The current density at the cathode should be between 5 and 10 amps. per square decimeter, or, if the electrodes are in the form of gauze, a "current concentration" of between 40 and 80 amps. per litre of solution should be used. The voltage should be 4 to 5. The current density at the anode is immaterial. With the above quantity of liquid, about 25 ampère hours of current should be passed through the bath. The product can then be analysed by titrating a sample with sodium nitrite. The remainder is subjected to steam distillation while still acid, to remove the unchanged nitrobenzene, and then saturated with soda, when the aniline can be distilled off.

The yield of aniline should be over 90% of the theoretical current yield.

(b) PREPARATION OF AZOBENZENE FROM
NITROBENZENE.

The reduction of nitrobenzene in an alkaline solution can, by means of the reactions shown above (p. 117) be made to proceed almost quantitatively into azobenzene. This may be expressed by the equation—



The cathode liquid, which is placed in a tall beaker, consists of 20 grams nitrobenzene and 5 grams crystallised sodium acetate in solution in 200 cc. alcohol (70 per cent.). The anode liquid consists of a cold saturated sodium carbonate solution contained in a porous cell placed inside the beaker. Nickel electrodes are used and a current density of 6 to 9 ampères per 100 square centimeters. The electrolysis is carried out at the boiling point, and after the theoretical amount of current has been supplied (17·5 ampère hours), the evolution of hydrogen begins immediately. The electrolysis is then continued for a few minutes longer, at a lower current density. The liquid is now free from nitrobenzene and contains azobenzene, together with a little hydrazobenzene and some azoxybenzene. A stream of air is then drawn through the liquid to oxidise the hydrazobenzene to azobenzene; the greater part of the latter then crystallises out in a pure state and can be filtered off. The remainder is precipitated

by addition of water, or is distilled over in steam, and can be purified by recrystallisation from alcohol or petroleum ether. The current efficiency of the process should be over 80 per cent., and the yield of material over 90 per cent. of the theoretical amount.

(c) TAFEL'S METHOD FOR STUDYING THE REDUCTION OF DIFFICULTLY REDUCIBLE SUBSTANCES IN SULPHURIC ACID SOLUTION.*

The investigations of Tafel referred to above are valuable contributions to the study of electrochemical methods of reduction. The reduction was first studied on a small scale in an experimental apparatus and the course of the process determined by measuring the volume of hydrogen evolved in the cathode portion of the cell under investigation, this being compared with the hydrogen evolved in a water voltameter placed in series with this cell. Thus, the amount of hydrogen evolved gives us an exact measure of the loss of the process in regard to the reduction.

Tafel investigated chiefly the reduction of such compounds as can only with extreme difficulty be reduced by ordinary chemical means. Strychnine, caffeine, succinimide and a number of other imides and amides were studied. The substances were always dissolved in a sulphuric acid solution, and it was found that reduction was only possible on

**Berichte*, xxxiii, 2209—2224 (1900).

Zeit. Physik. Chem., xxxiv, 187—228 (1900).

cathodes which possess a high overvoltage. Lead and mercury were the only metals found to be suitable for this purpose. Lead was chiefly employed on account of its convenience for working. Not only are such metals as platinum, silver, tin, copper, etc., incapable of producing the required reduction, but if present even in minute quantity (especially platinum) can altogether prevent the reduction taking place on lead electrodes.

For this purpose, therefore, it is essential that the lead used for the cathodes, as also the solutions employed shall be as free as possible from metallic impurities. The lead of which the electrodes are made should not contain more than 0.015 per cent. impurity.

The cathode consists of a cylinder of solid lead which is fixed by means of a rubber stopper into the porous cathode cell which is to contain the sulphuric acid solution of the substance to be reduced.

The anode is a sheet of lead, and the anode liquid a sulphuric acid solution.

To Prepare the Cathode. The metal cylinder is first cleaned and roughened by rubbing with sand and water, and then electrolytically oxidised by making it the anode, and using as electrolyte, a 20 per cent. sulphuric acid solution. A current density of about 2 amps. per 100 square cms. is used and the electrolysis allowed to proceed for half an hour. The cathode is then washed in cold water for some minutes, then dipped in boiling

alcohol and dried in a current of air. In this condition it can be kept for any desired length of time without suffering any change. On using as cathode in the reducing cell, the oxide is changed into spongy lead, a condition which is favourable to the reduction. The electrolytic oxidation of the surface is best repeated before each reduction.

The efficiency of the reduction process is favoured by the use of a low current density and high temperature.

The porous cell must be carefully cleaned in the following manner:—The new cell is allowed to stand for a long time in dilute caustic soda solution, and then washed by stopping up the top and drawing water through by means of a pump. Afterwards dilute hydrochloric acid is substituted for the water, and, finally, distilled water is forced through, and the cell dried at 100° .

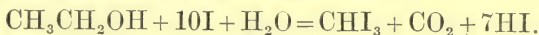
For the actual experiment two such cells are arranged in series, the gas delivery tube being brought so as to deliver the gas into two eudiometers.

The first cell is filled with sulphuric acid containing the substance to be reduced, whilst the second contains only sulphuric acid of the same strength.

2. ELECTROLYTIC OXIDATIONS.

(a) PREPARATION OF IODOFORM.*

Iodoform can be prepared by the action of free iodine upon a warm aqueous alkaline solution of alcohol according to the equation—



The hydriodic acid then reacts with the alkali to form an iodide.

The electrolytic method of preparation consists in electrolysing a solution containing potassium iodide, sodium carbonate, and ethyl alcohol, whereby the iodine set free at the anode reacts with the alcohol giving iodoform. A much better yield is obtained in this process than with the chemical method.

According to Elbs, the chemical method only gives a yield of 20—40 per cent. of the theoretical, the process being accompanied by the formation of a large amount of iodate, whereas, by the electrolytic method, an almost theoretical (about 98 per cent.) yield can be obtained. This is explained by Dony-Hénault as being due to the fact that in the latter method the smallest trace of iodine, which is liberated is in presence of a large

* Elbs and Hertz, *Zeit. Elek.*, iv, 113 (1897).

Förster and Mewes, *Zeit. Elek.*, iv, 269 (1897).

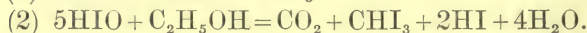
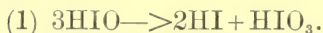
Dony-Hénault, *Zeit. Elek.*, vii, 57 (1900).

Elbs, "Electrolytic Preparations" (London, 1903).

excess of potassium iodide, which hinders the conversion of the hypoiodite into iodate. Moreover, in the electrolytic method the iodide which is formed during the reaction is capable of again yielding iodine by electrolysis.

The work of Dony-Hénault indicates that the formation of iodoform takes place in the following stages :—

The iodine liberated at the anode reacts with the hydroxyl ions (of which a large number are always present from the hydrolysis of the sodium carbonate) $\text{OH} + \text{I}_2 = \text{IO} + \overset{+}{\text{H}} + \text{I}^-$, whereby hypoiodite and iodide are formed. The HIO is unstable and breaks down in either of the following two ways :—

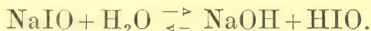


The yield of iodoform depends on the relative velocities of these two reactions. The presence of an excess of potassium iodide or iodate was found to hinder reaction (1), while the presence of free alkali favours this formation of iodate.

In support of the above theory, it was found by Dony-Hénault that a general parallelism existed between the conditions most favourable for the formation of hypoiodous acid and for iodoform, and it was shown that a solution of this acid (free from iodine) when added to alcohol gave iodoform according to equation (2) above.

During the electrolytic method of preparation

hypoiodous acid is formed from sodium hypoiodite by hydrolysis, thus :



Practical. The following are the best conditions for preparing iodoform :—

Anode Liquid: 100 grams water, 5 grams sodium carbonate, 10 grams potassium iodide, 20 cc. ethyl alcohol.

This liquor is placed in a porous cell inside a beaker. The beaker also contains the cathode liquor consisting of a solution of sodium carbonate.

The cathode consists of a nickel, and the anode, a platinum electrode.

The current density at the anode should not be above 1 amp. per sq. cm., and the temperature should be maintained at 60°.

During the electrolysis the solution tends to become alkaline, as, according to the equation above (p. 123), 10 equivalents of sodium hydrate are formed to 7 of hydriodic acid. To neutralise the sodium hydrate, a slow current of carbon dioxide should be passed through the anode liquid during the electrolysis.

In order to obtain any considerable yield of iodoform, the electrolysis should be continued for 2 to 4 hours, when, on cooling, the iodoform separates out in the crystalline form. The yield should be calculated from the amount of current which has passed through the cell as measured by the copper voltameter, and by making use of the equation above. The process can be made continuous by removing, every few hours, the iodo-

form formed and adding alcohol, carbonate, and iodide to make up for that decomposed.

It is not possible to prepare the analogous bromoform and chloroform by the method described above for iodoform, as in these cases aldehydes and other oxidation products of alcohol are given on electrolysis. This is due to the fact that the decomposition potential of iodine from a potassium iodide and soda solution is only 1.12 (the normal hydrogen electrode being taken as zero), whilst oxygen separates at 1.7. With potassium bromide, alcohol and sodium carbonate bromine separates at 1.75 volt. and with potassium chloride, chlorine at 2.1 volts.*

(b) PREPARATION OF SODIUM HYPOCHLORITE.†

A solution of common salt, of a concentration of 150 to 200 grams per litre, is taken as the electrolyte, and placed in a glass vessel, which can be efficiently cooled on the outside by ice-water. Platinum electrodes are used, and some arrangement made to secure a good circulation of the electrolyte. The current density at anode and cathode should be 15 amps. per square decimeter. The temperature must not be allowed to rise above 25°. At the cathode, hydrogen is evolved, but at the anode hardly any gas is evolved at first, as the chlorine which is liberated, dissolves in the water

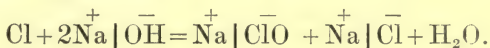
* Wohlwill. *Zeit. Elek.*, v, 52.

† Elbs, "Electrolytic Preparations," p. 21.

E. Abel, *Hypochlorite und Elektrische Bleiche* (Knapp, Halle).

F. Oettel, *Zeit. Elek.*, i, 69, 356, 474; vii, 315, 449.

and reacts with the alkali, formed at the cathode, to form hypochlorite, thus:—



After the electrolysis has proceeded for some time, oxygen is given off in increasing amount. This is due to the liberation of ClO^- ions together with the Cl^- . Thus: $2\text{ClO}^- + \text{H}_2\text{O} + 2\oplus = 2\text{HClO} + \text{O}$.

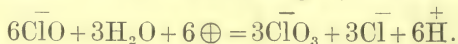
The amount of ClO^- which takes part in the electrolyte is proportional to the quantity present, and also varies with the current density. The ClO^- ions are discharged at a somewhat lower potential than the Cl^- , but as the latter are always present in a much larger quantity than the former, by working with a high current density, relatively fewer ClO^- ions are discharged, as less time is given for their migration to the electrode. Moreover, a high current density at the cathode diminishes relatively the reduction of the hypochlorous acid by the hydrogen, as a given volume of this gas is in contact with a smaller quantity of electrolyte.

After the hypochlorous acid has reached a certain concentration, the reduction at the cathode by the hydrogen liberated becomes much more marked, so that it is not practicable to prepare a solution of a higher concentration than about 14 grams of sodium hypochlorite per litre.

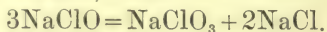
The current yield is at first over 90 per cent., and sinks gradually to below 30 per cent. The

current yield can be increased and more concentrated solutions prepared by adding about 0.1 per cent. of calcium chloride or alkali chromate. These substances cause a thin coating to take place on the cathode, which is very effective in preventing reduction of the hypochlorous acid by the hydrogen.

The progress of the electrolysis can be measured by passing the current in series through a water voltameter, and by surrounding the electrodes in the hypochlorite vessel with glass cylinders, so that the volumes of gas evolved can be measured. The amount of hydrogen liberated at the cathode should correspond to the amount in the water voltameter. Any deficiency in the former indicates reduction of the hypochlorous acid. The oxygen evolved at the anode represents the loss through liberation of the ClO^- ions. In addition to these sources of loss, a certain amount of chlorate is formed at the anode by deposition of ClO^- ions in accordance with the following equation:—



If the temperature of the bath is allowed to rise above 25° this change of hypochlorite into chlorate and chloride takes place throughout the electrolyte to a certain extent, thus:



The amount of hypochlorite in the product can be determined iodometrically.

A good circulation of the electrolyte is necessary,

so that the acid formed at the anode is neutralised by the alkali at the cathode, or else the accumulation of the H^+ ions will cause the hypochlorous acid to decompose, as represented by the equation $\text{H}^+ + \text{Cl}^- + \text{HClO} = \text{Cl}_2 + \text{H}_2\text{O}$, or, in other words, hypochlorous acid is decomposed by hydrochloric acid into chlorine and water.

The formation of hypochlorite, by the electrolysis of a salt solution, is represented above as arising from a secondary chemical effect of the liberated chlorine on the alkali formed at the cathode. The action can, however, be equally well represented as taking place more directly by the following ionic changes* :—

At the anode $\text{Cl}^- + \text{H}_2\text{O} + 2 \oplus = \text{ClO}^- + 2\text{H}^+$.

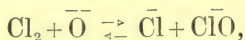
At the cathode $\text{H}_2\text{O} + 2 \ominus = \text{O}^{2-} + \text{H}_2$.

According to this view, the formation of hypochlorite consists in the addition of an electrically neutral oxygen atom on to the Cl^- ion. To effect this oxygen must be separated under conditions which enable combination with the Cl^- ion to take place. For this purpose, the pressure of the separated oxygen must be greater than the "oxygen pressure" of the hypochlorite in solution. The former value varies with the potential difference at the anode, and the latter depends on the ratio of the hypochlorite to chloride in solution (see p. 106).

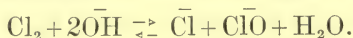
The electrolytic formation of hypochlorite can

* Cf. Foerster and Müller, *Zeit. Elektroch.*, 1903, ix, 171.

also be regarded as the addition of chlorine on to the $\bar{\text{O}}$ ion, thus: $2\bar{\text{Cl}} + 2\oplus = \text{Cl}_2$

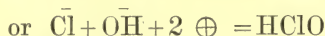


or, taking hydroxyl instead of oxygen ions,

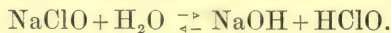


The reaction may also be expressed as consisting of a simultaneous discharge of $\bar{\text{OH}}$ and $\bar{\text{Cl}}$ ions.*

Thus, $\bar{\text{Cl}} + \bar{\text{O}} + 2\oplus = \bar{\text{ClO}}$, or, in the case of hydroxyl ions,



The more effective bleaching property of sodium hypochlorite prepared electrolytically over that obtained from ordinary bleaching powder which always contains an excess of alkali, probably depends on the existence of free hypochlorous acid in the former. This is given by the hydrolysis of neutral sodium hypochlorite, thus:



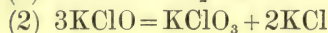
(c) PREPARATION OF POTASSIUM CHLORATE. †

The electrolytic preparation of chlorate is based on the same reaction as in the usual chemical method of preparing this substance, which can be expressed by the following equations:—

* Cf. Haber, *Zeit. Anorg. Chemie*, xvi, 1898, 198, 329.

† Müller, *Zeit. Elek.*, v, 496.

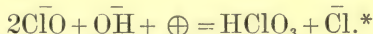
Foerster and Muller, *Zeit. Elek.*, viii, 515, 633, 665.



The second reaction does not take place below a temperature of 20—30°, but at higher temperatures is complete.

During the electrolysis of a potassium chloride solution, at the anode we have $2\bar{\text{Cl}} + \oplus = \text{Cl}_2$, and at the cathode $2\bar{\text{K}} + 2\text{H}_2\text{O} + \oplus = 2\text{KOH} + \text{H}_2$.

The chlorine then reacts with the potassium hydroxide according to the above equations. In addition to this secondary formation of chlorate, a primary action also probably takes place by the simultaneous discharge of $\bar{\text{OH}}$ and $\bar{\text{ClO}}$ ions, as expressed in the equation—



And also by the union of nascent oxygen, which is liberated at the anode, on $\bar{\text{ClO}}$ ions present in solution, thus: $\bar{\text{ClO}} + 2\text{O} = \bar{\text{ClO}}_3.†$

The following have been found to be the best conditions for conducting the preparation of potassium chlorate. Platinum is the most suitable metal for the anode. The addition of a chromate increases the yield, probably on account of the formation of a skin of chromium hydrate on the surface of the cathode, which protects the oxidised

* Wohlwill. *Zeit. Elektroch.*, v, 52.

† Cf. Lorentz and Wehrlin, *Zeit. Elektroch.*, viii, 515, 633, 655.

salt from the reducing action of the hydrogen liberated.

A current of carbon dioxide should be passed through the solution during electrolysis, so as to cause circulation of the electrolyte and neutralise the free alkali which is formed. The slight acidity produced by the carbon dioxide facilitates the formation of free hypochlorous acid.

A sufficiently large volume of the electrolyte in proportion to the current density, should be taken in order to give the secondary actions time for completion.

A temperature of at least 40° should be employed in order to secure the formation of chlorate, to keep the resistance of the bath low, and to prevent the formation of perchlorate. At lower temperatures this formation of perchlorate takes place by the union of two discharged chloric acid ions with water thus: $2\text{ClO}_3 + \text{H}_2\text{O} = \text{HClO}_4 + \text{HClO}_3$.

At higher temperatures liberation of ClO_3^- ions takes place at the anode to give oxygen and reform chloric acid, thus: $2\text{ClO}_3 + \text{H}_2\text{O} = 2\text{HClO}_3 + \text{O}$.

The amount of this wasteful oxygen evolution of course depends on the concentration of the chlorate in solution. (Compare similar case with hypochlorites.)

Practical.

Electrolyte: 100 grams potassium chloride, 1 gram potassium carbonate, 1 gram potassium dichromate dissolved in 250 cc. warm water.

Electrodes. Platinum Foil. Current density:— at anode, about 10 amps. per square dm.; at cathode, somewhat greater than at anode; distance apart of electrodes, 1 cm.

The temperature is kept between 40° and 60°, and a slow current of carbon dioxide passed through the solution during the electrolysis.

At least 60 ampère hours must be passed through, since 1 amp. hour only yields 0.75 gm. potassium chlorate.

During the cooling potassium chlorate separates out, and a further quantity is obtained by concentrating the solution. This is purified by recrystallisation, and a current yield of 70 to 80 per cent. should be obtained.

The amount of chlorate, together with hypochlorite in solution, can, at any time, be estimated by boiling a sample with ferrous sulphate and sulphuric acid, whereby the chlorate is reduced. The amount of ferrous sulphate left is then determined by titration with permanganate in presence of manganese sulphate.*

* For a more exact method of determining these substances, see Wohlwill, *Zeit. Elektroch.*, v, 64.

PART III.

PYROMETRY.

1. THERMO-ELECTRIC PYROMETRY.

Calibration of a Thermo-junction. Thermo-electric pyrometry is based on the discovery of Seebeck, that if two separate metals are allowed to touch at two different places, and if these points of contact are at different temperatures, an electromotive force is generated.

This effect was first systematically studied and made use of for the measurement of high temperatures by Becquerel, Regnault, and Le Chatelier.

Couples formed of different metals show very great variations in the E.M.F. generated at their junctions with change of temperature. Most metals show irregularities due to changes which take place in their physical condition on heating, and which cause the generation of parasitic currents through contact E.M.F.'s generated in the regions of intermediate temperature.

The metal which is most free from such objections is platinum and its alloys with rhodium and iridium. A source of error which is apt to arise even in these cases is due to inequality in the annealing. The drawing and even subsequent

twisting of the wire produces a hardening, so that it is important that the wires should, before use, be well annealed by raising to a white heat.

Further, after prolonged use, especially at high temperatures, physical changes, such as crystallisation of the metal, take place, which affect the E.M.F.

Avenarius and Tait showed that, up to 300° , the E.M.F. of a large number of couples could be expressed by means of the formula :

$$e = a(t - t_0) + b(t^2 - t_0^2),$$

where t is the temperature of the hot and t_0 of the cold junction. Le Chatelier showed that this formula also applied at higher temperatures.

Holman showed that when the cold junction was at zero the E.M.F. of thermo-couples could be expressed by the following logarithmic formula : $e = mt^n$, or $\log e = n \log t + \log m$; so that, in a graph, $\log t$, plotted against $\log e$, gives a straight line.

The results obtained by Le Chatelier for a thermo-couple of platinum and platinum—10 per cent. rhodium satisfy the equation :—

$$\log e = 1.2196 \log t + 0.302,$$

where e is expressed in microvolts (millionths of a volt). Different values for these constants will be obtained, however, for wires drawn from different ingots of metal, if there are any variations in the chemical composition.

A number of precautions have to be taken when using the thermo-junction in practice. The metal wires must not be exposed, at a high temperature, to a reducing atmosphere, as most metals are more

or less volatile and attack platinum very rapidly. The same applies to gaseous compounds of carbon, phosphorus, and silicon. In an oxidising atmosphere these metal vapours and other deleterious substances are mostly rendered non-volatile. Contact of the platinum with silica and silicates should in all cases be avoided, or the metal will be slowly attacked. The platinum should not be exposed to a temperature above $1300-1400^{\circ}$ for a prolonged period, even in an oxidising and clean atmosphere, or it will gradually become brittle, due, in all probability, to crystallisation. This change will not only tend to cause an error in the E.M.F. generated through parasite currents, but will ultimately lead to the breaking of the wire.

If the thermo-junction is to be used in the neighbourhood of any substances which can act deleteriously on the platinum, the wires must be carefully enclosed in a tube of silica, magnesia or other suitable refractory material.

The E.M.F. generated, which serves as a measure of the temperature, can be measured either (1) by means of a potentiometer, or (2) by means of a high resistance galvanometer or millivoltmeter.

The Potentiometer Method. The potentiometer gives an absolute measure of the E.M.F. of a junction. In this method, the E.M.F. of the couple is exactly balanced by an E.M.F. which can be accurately adjusted and measured. A sensitive galvanometer is used to indicate the position of balance. In some types of potentiometer

meter, by attaching a series of resistances to dials, the resistances are arranged so that the dial readings give the E.M.F. directly in decimals of a volt. A simple type of potentiometer can be arranged as shown in Fig. 23.

A storage cell at W is placed in series with a rheostat R and a series of coils, or combination of coils and bridge wire represented by $A B$. A standard cell of known E.M.F. is connected to

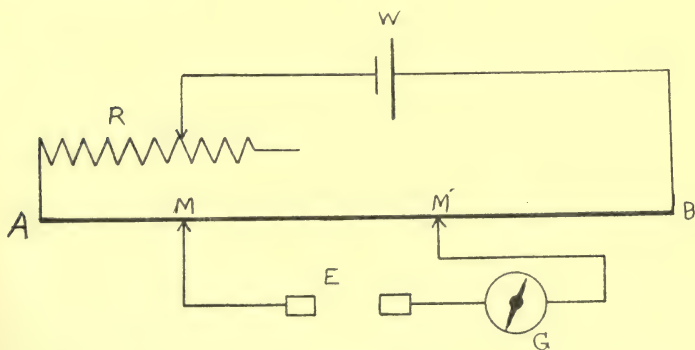


Fig. 23.

A and B , and the resistance R so adjusted that no current passes through the galvanometer. The cell is then removed and the leads from the thermocouple are connected at points along the slide wire M and M' in such a way that the E.M.F. from the thermo-junction is exactly balanced by the opposing E.M.F. from W . This position of balance is indicated by the galvanometer G .

If the E.M.F. of the standard cell is E and that

of the thermojunction e , we have the following relation: $e = E \frac{MM'}{AB}$

Galvanometric Method. In this method the E.M.F. of the thermo-junction is read directly by means of a galvanometer. This method is not strictly accurate, since the deflection of the galvanometer depends on the total resistance of the circuit, and that of the thermo-junction wires varies with the temperature and other changes. However, by arranging the galvanometer resistance to be very high, in comparison to that of the thermo-junction, this source of error can be reduced to a very small amount, and for most practical purposes the method can be made to give a sufficiently great accuracy, and is far more convenient for temperature estimation than the potentiometer method. The galvanometer used can be calibrated directly in millivolts.

Precautions in taking readings. The resistance of the galvanometer should be at least 200 ohms for use with the ordinary platinum thermo-couples, and the temperature coefficient should be negligible.

There should be no secondary source of E.M.F. present. The galvanometer should be carefully levelled during the readings, and the zero of the instrument should remain constant. (If the temperature of the cold junction is not at zero, then the temperature indicated will be low by about $\frac{T}{2}$, where T is the actual temperature of the cold junction and less than 30° .)

The junction of the two wires should always be fused (by means of an oxyhydrogen flame), instead of twisted, as in the latter case, an uncertain resistance always occurs, which, in the galvanometric method may lead to serious error. Moreover, in accurate work, a twisting of the wire may lead to inequalities in the hardness of the metal and cause the generation of parasite currents in regions of lower temperature.

Calibration of the Thermo-junction. According to the Holman formula, $\log e = n \log t + \log m$. It is therefore only necessary to calibrate the thermo-junction at two fixed points in order to evaluate the constants in the equation.

For the sake of accuracy, the fixed points chosen should be as far apart as possible, and an intermediate point may be taken so as to verify the results. The two most convenient fixed points are the melting point of zinc (420°), and of copper (1084° in a reducing atmosphere). The melting point of aluminium (655°) may be conveniently taken as an intermediate point. In carrying out a calibration at the melting point of any of these metals, a quantity of the metal is placed in a fire-clay crucible, where it can most conveniently be melted by heating in a muffle furnace. The molten metal is covered with a layer of carbon so as to maintain a reducing atmosphere, and its temperature taken considerably above the melting point. The thermo-junction wires are carefully enclosed in a suitable refractory tube, which is

inserted in the mass of molten metal, the heating of the furnace having been stopped.

The metal is allowed to stand and cool slowly, and temperature readings are taken at regular short intervals.

When the point of solidification is reached, the temperature will remain constant over a long interval. The constancy of temperature of the metal during this interval will also give an indication of the purity of the metal used. When the metal has all solidified, the temperature should again fall quite regularly.

The value of $\log e$ and $\log t$ should then be plotted as a straight line, and from this a curve should be constructed showing the relation of e to t .

2. RADIATION PYROMETRY.

Optical and radiation pyrometry are based on the measurement of the energy which is radiated from heated bodies, either in the form of visible light, or the total radiations consisting chiefly of heat waves in the infra red part of the spectrum. This method of pyrometry is particularly suited for high temperature measurements as the intensity of radiation increases enormously with the temperature. For use in practice, such methods possess the great advantage that all parts of the recording instruments are placed at a considerable distance from the heated body, and no part is exposed to any high temperature. For this reason

the apparatus undergoes no deterioration with use and no alteration to the constants of the instruments is experienced, through physical and chemical changes which all substances undergo at high temperatures.

At temperatures above the melting point of platinum there is at present no other method of pyrometry available. The optical temperature scale is based on radiation laws as formulated by Wien, Paschen, and Planck. At temperatures up to about 1800° the value can be directly compared with the platinum scale, but above this temperature cannot be reduced to any of the other scales, and the values are subject to the applicability of the various radiation formulæ at very high temperatures.

The increase in luminous radiation from a heated body, with rise of temperature, was measured photometrically by Lummer and Kurlbaum.* The radiating body consisted of platinum in cylindrical form, and the intensity of light emitted was found to satisfy the following formula:—If I_1 and I_2 are the intensities of the light radiated at the temperatures T_1 and T_2 respectively, the two temperatures being taken close together, then $\frac{I_1}{I_2} = \left(\frac{T_1}{T_2}\right)^x$

At 900° (abs.) x was found to have the value 30, and at 1900° , 14. These measurements were

* *Ver. d. Deutsch. Phys. Ges.*, 1900, ii, p. 89.

further extended by Rasch,* who found that the product $T\lambda$ gives an approximately constant value, 25000.

According to this formula, it is seen that at 900° abs. the light emitted increases 30 times as rapidly as the temperature, and at 1400° abs. 14 times as rapidly. The increase of radiation with temperature is also a function of the wave length; for shorter waves it is greater, and for longer waves less.

It is the very great increase in luminosity of a body on rise of temperature that makes it possible for experienced persons to gauge the temperatures by mere observation of the colour.

An important source of error has here to be considered in applying radiation measurements for the estimation of temperatures. The radiation from a body depends not only on its temperature, but on the nature of the substance and the condition of its surface. Thus different substances at the same temperature may emit largely different quantities of energy.

The intensity of radiation from incandescent iron or carbon, for instance, at 1000° is several times greater than that from polished platinum. At the melting point of platinum (1750°), the radiation of red light from this metal has been found to be equal to that from a substance which gives "black body" radiation at 1540° , thus showing a departure of 210° . This discrepancy is

* *Ann. d. Phys.*, xiv, 193, 1904.

less at lower temperatures. The departure from black body radiation varies in different parts of the spectrum. When light falls on a substance a certain amount is absorbed or transmitted, and the remainder reflected, so conversely when the body is rendered luminous, the same proportion which in the above case was absorbed is now emitted, and the remainder diffused, *i.e.*, absorbed or retained.

Kirchoff introduced the conception of a "black body," which he defined as one which would absorb all the radiations falling on it, and neither reflect nor transmit any, and on being heated would emit the maximum radiation. He further pointed out that the radiations from such a body are a function of the temperature alone and that these conditions of "black body" radiation exist in the interior of any enclosure all the sides of which are at a uniform temperature.

Wien and Lummer devised a laboratory apparatus in which these conditions are fulfilled by heating the walls of a hollow opaque enclosure as uniformly as possible, and observing the radiation coming from the inside through a very small opening in the walls of the enclosure.

Stefan and Boltzmann investigated the relation between the radiation and the temperature of a black body, and formulated the law that *the total radiation is proportional to the fourth power of the absolute temperature*. Thus, if E denotes the radiation from a body at temperature T_1 to one at T_0 , then $E = K(T_1^4 - T_0^4)$.

TOTAL RADIATION PYROMETERS.

When the method of measuring the temperature is based on the total radiation emitted from the hot body, an important precaution has to be observed. By far the largest part of the energy radiated from a heated body is in the infra red part of the spectrum, and it is important that no absorption of these rays should occur by any part of the apparatus through which they have to pass. Glass, on account of its non-permeability to infra red rays, cannot for this reason be used anywhere in the field of view. In the case of the Féry pyrometer the lenses are made of fluorite, a substance which gives only one small absorption band in the infra red. The rays from the incandescent body are focussed on to a small thermo-junction, when the E.M.F. generated is a function of the temperature of the radiating body. It is also necessary for a correct measurement that the area of the surface of the incandescent body should not be below a certain size in relation to the distance from the pyrometer so that the focussed rays may completely cover the thermo-junction. This method of pyrometry is also subject to the limitations caused by departures from "black body" radiations.

3. OPTICAL PYROMETRY.

*The Wanner Pyrometer.**

In the Wanner pyrometer the temperature is estimated by measuring the intensity of radiation of light from one particular part of the spectrum.

The relation between the temperature and the intensity of the light of any particular wave length can be expressed by a formula which was deduced by Wien.† According to this,

$$I = c_1 \lambda^{-5} e^{\frac{-c_2}{\lambda T}}$$

This formula has been confirmed by experimental work done by Paschen,‡ and by further deductions by Planck.§

This formula can be expressed in a simpler form

$$\text{as: } \log I = K_1 - K_2 \frac{1}{T}$$

where $K_1 = \log c_1 - 5 \log \lambda$ and $K_2 = c_2 \frac{\log e}{\lambda}$

As the Wanner pyrometer is usually constructed red light of wave length 0.656μ is used. This is compared photometrically with the light radiated from a standard lamp of constant intensity. Rays of light from the two sources enter the pyrometer side by side, and after passing through a direct vision spectroscope the red rays from each traverse

* Wanner, *Phys. Zeitsch.*, iii, 112 (1902).

† *Ber. K. Akad. Wiss.*, Berlin (1893), p. 55.

‡ *Wied. Ann.*, lviii, 455 (1896).

§ *Ann. d. Phys.*, ii, 141 (1900).

a Rochon prism where they are polarised in directions at right angles to each other. A Nicol analyser is placed before the eyepiece, and by rotating the prism, the intensity of the light from one source is increased, and that from the other diminished. On sighting through the pyrometer the light from the two sources is found to illuminate the two respective halves of the field, and the Nicol analyser is rotated until the two halves are equally bright, when the field appears to be uniform. The degree of rotation necessary to produce this uniformity gives a measure of the temperature of the incandescent object.

As shown in Fig. 24, light from the standard lamp enters the slit S_1 , after diffuse reflection from a right-angled prism placed before S_1 , while light from the object whose temperature is to be measured enters the slit S_2 . These two beams of light are rendered parallel by the lens O_1 , and, by means of the direct vision spectroscope, the rays are resolved into a continuous spectrum. The Rochon prism R then separates each beam into two beams polarised at right angles to one another. The light now traverses the biprism B , which is constructed with such an angle that the red light of two images only of opposite polarity falls on the slit D . This biprism increases the number of images to 8, but the remaining 6 are cut off from the slit D . If, now, the analyser A is inclined at an angle of 45° to each polarised beam, and if the intensities of the light entering S_1 and S_2 are equal, then the field seen through the eyepiece

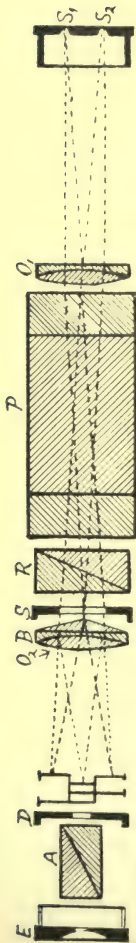


Fig. 24.

will appear of uniform brightness. If, however, instead of 45° , the Nicol is placed at an angle ϕ the following relation holds:—

$$\frac{I}{I_0} = \tan^2 \phi \cdots \cdots (a)$$

where I equals the intensity of light through S_2 from the body whose temperature is to be measured, and I_0 equals that through S_1 from the standard source.

Since monochromatic light is used, the basis of the calibration of the Wanner pyrometer is given by Wien's equation:—

$$\log \frac{I}{I_0} = \frac{c_2}{\lambda} \log_{10} e \left(\frac{1}{T_0} - \frac{1}{T} \right) \cdots \cdots (b)$$

where T_0 and T are the absolute black body temperatures of the standard source and the incandescent body respectively.

For a "black body" the constant c_2 has been evaluated at 14500, and as the instrument is usually constructed $\lambda = 0.656 \mu$.

According to this formula, all the data necessary for the calibration of the instrument is a knowledge of the apparent black body temperature of the standard source, and the reading of the analyser at the normal point when $I = I_0$. Any other temperature can then be calculated by use of the above two formulæ (a and b).

It is very important to be able always to reproduce the comparison light at S_2 of constant intensity. A small filament lamp is used for this purpose, and the current passing through is controlled by a regulating resistance, and is measured

by an ammeter. It is necessary to frequently check and readjust the intensity of this comparison source. For this purpose use is made of an amyl acetate lamp, burning under carefully regulated conditions, on the flame of which the pyrometer is sighted. Setting the Nicol at 45° , the electric comparison lamp is then adjusted in brightness until the light from both sources is uniform. The apparent "black body" temperature of the flame is evaluated by sighting the pyrometer with the Nicol in the same position on to a substance which gives "black body" radiation, and whose temperature can be regulated and measured by some standard means.

The arrangement of the apparatus for the purpose of standardisation by the amyl acetate lamp is shown in Fig. 25. C is the incandescent lamp, L the leads to the battery, the current passing through the ammeter A and the regulating resistance R. A ground glass diffusing glass is placed at D in between the flame and the slit of the pyrometer. F is the flame gauge. It is very important that the ground glass diffusing screen should always be placed in exactly the same position relative to the flame and the slit S_2 , and that it is free from any dust, etc. The amyl acetate lamp should be allowed to burn for five minutes before the readings are taken, and the height of the flame should be adjusted so that the tip is about 1 mm. above the level of the flame gauge F. The incandescent lamp should also have the current

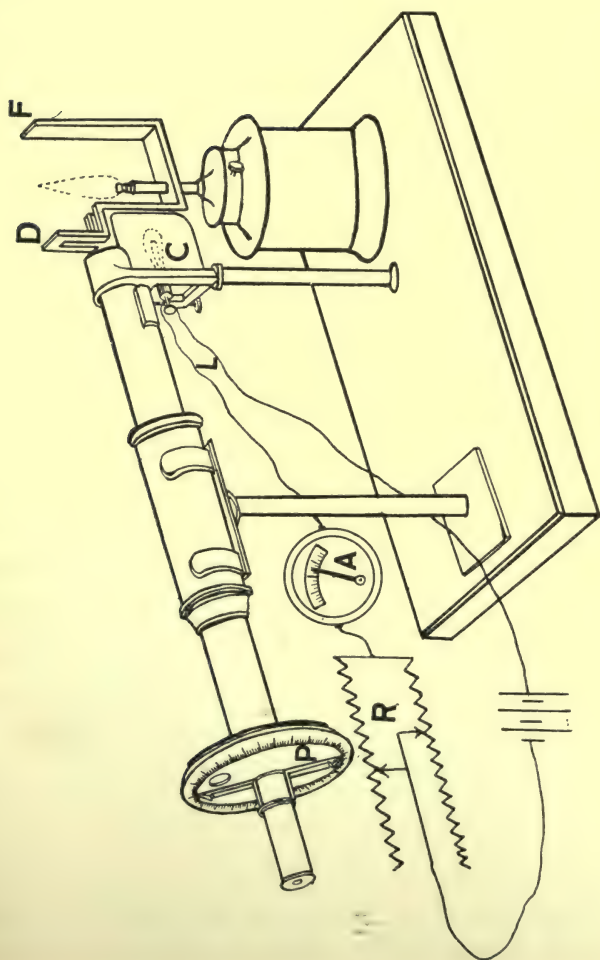


Fig. 25.

passing through for a few minutes before a reading is taken.

For subsequent measurements of temperature, the pyrometer is removed from the stand and sighted directly on to the incandescent body.

The Nicol analyser has a pointer (P) attached, and a scale graduated in degrees. By referring to tables the temperature is ascertained directly from the scale readings. The sensibility of the instrument is greatest when the analyser is at the normal position, which corresponds to the black body temperature of the amyl acetate flame when viewed through the diffusing screen (this is 1150° as usually constructed). The sensibility is as follows :

0.1 scale division	=	1°	at	1000°
0.1	,,	,,	=	2° ,, 1500°
0.1	,,	,,	=	7° ,, 1800°

For higher temperatures a smoked glass of known absorption is placed in front of the slit S_1 , and another tabulation of the temperatures corresponding to the position of the Nicol in this case is provided.

The coefficient of absorption of the smoked glass is given by the following formula :—

$$\log_{10} K = \log_{10} \frac{I_1}{I_2} = \frac{c_2}{\lambda} \log_{10} e \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

where K is the coefficient of absorption and T_1 and T_2 are the apparent "black body" temperatures (abs.) sighted first without and then with the

smoked glass. Since $C_2 = 14500$ and $\lambda = 0.65 \mu$ then the above formula reduces to

$$\log_{10} K = 9983 \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\text{or } \frac{1}{T_2} - \frac{1}{T_1} = \frac{\log_{10} K}{9983} = C.$$

This constant C can thus be calculated by measuring the absorption at any one temperature.

There is no necessity to focus the Wanner pyrometer for varying distance from the object, and no definite image of the object is formed in the eyepiece. If the incandescent body is not sufficiently large to cover the half field of the pyrometer at the particular distance it is placed from the instrument, the alteration in the intensity is only very small, though in this case the adjustment to uniformity with the other portion of the field is rendered more difficult.

This method of pyrometry also possesses the great advantage that when clear glass, mica or quartz intervene in the path of the rays, the absorption of the red light only causes a slight error in the temperature indicated, and for most purposes this can be neglected.

If the glass is not very clear the real temperature (T_1) (abs.) is calculated from the apparent temperature (T_2) by means of the formula :

$$\frac{1}{T_1} = \frac{1}{T_2} - C.$$

The constant C is calculated by taking a temperature reading of an incandescent object at

any constant temperature—1st, directly, and, 2nd, through the transparent medium. In these temperature measurements, care must be taken that the atmosphere surrounding the heated object is free from fumes, or very large errors may arise through absorption.

Calibration of an Optical Pyrometer.

The readings of an optical pyrometer can be conveniently calibrated by sighting on to a heated substance which radiates as a “black body,” or with which the amount of departure from this radiation is known, and the temperature of which is simultaneously measured by some other standard method. For temperatures up to 1200—1300° the radiation from a heated enclosure (which radiates as a black body) may be made use of. The most convenient form of apparatus is an electric furnace, as shown in Fig. 26. The central porcelain tube is wound with platinum wire (W) (or wire consisting of some alloy of a high melting point, such as “Nichrome”), and the space between this and the outside case is filled with magnesia or kieselguhr. A plug of magnesia or other refractory material is placed at P, and is provided with two holes to allow the wire of a thermo-junction to pass through, the junction being made at K. The interior of the furnace can be slowly raised to incandescence by the passage of an electric current through the wire coil. It is necessary that the temperature should be uniform for some distance in the neighbourhood of the diaphragm,

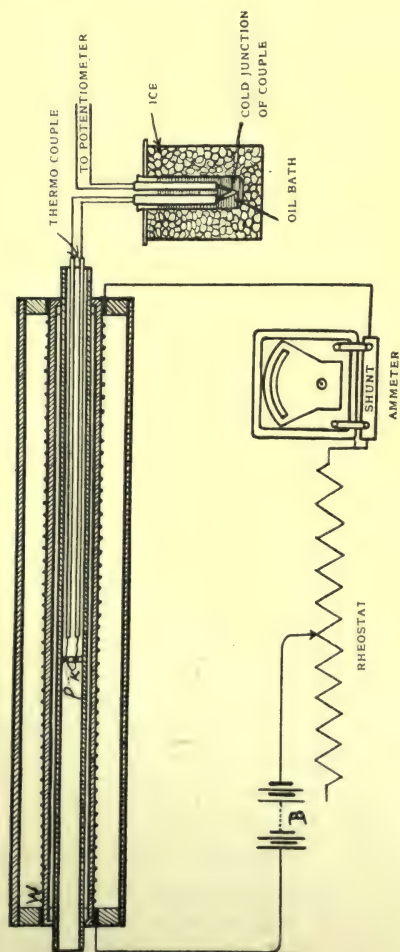


Fig. 26.

and when the thermo-junction wire is at the same temperature it becomes invisible against the bright background.

The pyrometer is sighted into the porcelain tube, and the temperature is given by the thermo-junction which is connected with a potentiometer or high resistance galvanometer.

At higher temperatures a calibration can be made at certain fixed points by sighting the pyrometer on to a strip of pure platinum, rhodium or iridium, which is gradually heated to its melting point by means of a carefully regulated current. The apparatus for this calibration is shown in Fig. 27. The brass tubes A and B, which can be cooled by water circulation, have small clamps attached at C and D. In this way a strip of metal (S) of 4 to 6 cms. long and about 4 mms. diam. can be connected between the tubes, so as to form electrical contact. The current leads are connected at M and N, and a slow current of water is allowed to pass through the tubes *w, w*.

During the heating of the strip means must be taken to shield it from draughts of air which would tend to cause fluctuations of the temperature. The vicinity of any other bright light which would cause an error through reflection must also be avoided. The current through the strip is carefully regulated by a suitable rheostat and measured by an ammeter. Sometimes the metal does not heat uniformly, and this is more apt to occur with a long than with a short strip. In this case, however, the place of highest temperature can easily be

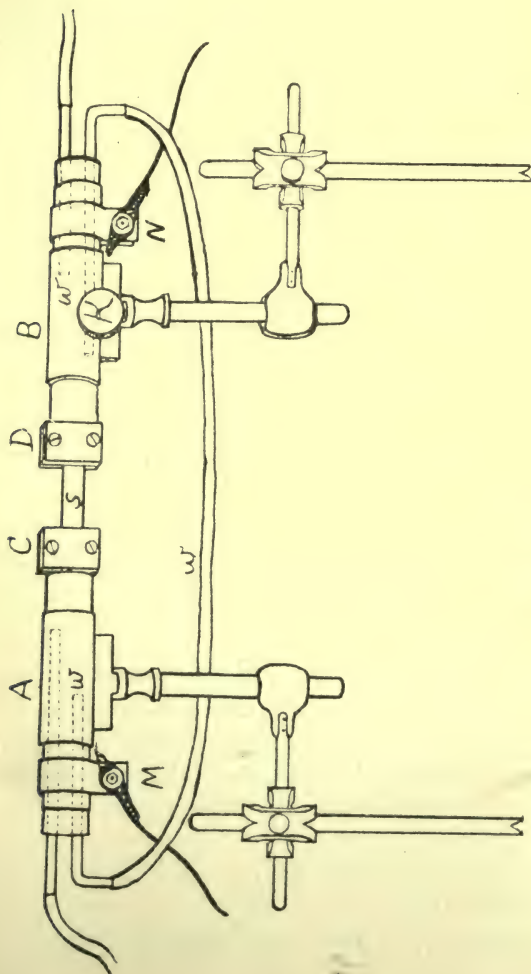


Fig. 27.

found by moving the pyrometer from side to side. The temperature is very gradually and continuously raised and the pyrometer continually readjusted until the metal fuses.

It is necessary that the surface of the strip should always be placed in a "normal" position relatively to the pyrometer, *i.e.*, the whole surface of the metal must be at right angles to the axis of the pyrometer. For this reason, as the metal expands with the rising temperature the extension should be taken up by rotating the screw K, which works a rack and pinion and increases the distance between A and B. For red light, the apparent "black body" temperature of platinum at its melting point has been found by Waidner and Burgess to be 1541° .*

Holborn and Henning† found the "black body" melting point of platinum to be 1545° , rhodium 1650° , and iridium 2000° .

Departure from Black Body Radiation.

Waidner and Burgess (*loc. cit.*) measured the radiation from various substances at different temperatures and found the following values in the case of red light ($\lambda = 0.65 \mu$):—

* "Optical Pyrometry," Bull. Bureau Standards, Washington, No. 2, 1905.

† *Sitzungsber. K. Akad. Wiss.*, Berlin, 1905, xii, 311.

For platinum :

At 1750° departure from B.B. radiation			corresponds to 209°
„ 1500°	„	„	126°
„ 1215°	„	„	96°
„ 1064°	„	„	91°
„ 782°	„	„	65°
„ 723°	„	„	57°

For iron oxide :

At 770° departure	corresponds to	23°
„ 980°	„	46°

For fine grained Battersea crucible :

At 770° departure	corresponds to	14°
„ 1050°	„	54°

For copper oxide :

At 750° departure	corresponds to	25°
„ 1065°	„	49°

For unglazed porcelain :

At 730° departure	corresponds to	30°
-------------------	----------------	-----

It has been shown that the radiation from graphite at 1250° is equal to the radiation from a black body to within 10°.*

Holborn and Henning† made a series of measurements on the radiation from the noble metals at different temperatures, and conclude from these results that, for each method, $\frac{E_m}{E_s}$, the ratio of the light emitted by the metal to that

* Greenwood *Trans. Chem. Soc.* (1908), xciii, 1486.

† *Loc. cit.*

which is emitted by a black body at the same temperature, is a constant for all temperatures;

$$\text{thus: } \log \frac{E_m}{E_s} = \log_{10} e \frac{14500}{\lambda} \left(\frac{1}{T} - \frac{1}{M} \right)$$

where T is the black body temperature and M the apparent temperature of the metal.

Hence $\frac{1}{M} - \frac{1}{T} = C$ where C is a constant.

The following values were found for $\frac{E_m}{E_s}$ and for C , with the different metals for red light:—

	$\frac{E_m}{E_s}$.		C .
Platinum ...	0·319	...	0·0000507
Gold	0·127	...	0·0000916
Silver	0·080	...	0·0001119

APPENDIX.

TABLE OF RELIABLE MELTING AND BOILING POINTS.

Liquid Hydrogen	-253°
„ Oxygen	-182°
Freezing Mercury	-39°
Melting Ice	0°
Boiling Point of Aniline at 760 mm. press.						184°
„ Naphthaline				„		220°
„ Diphenylamine				„		302°
„ Sulphur				„		445°
Melting Point of Tin	232°
„ Zinc	419°
„ Antimony	632°
„ Aluminium	657°
„ Sodium Chloride	800°
„ Silver (in air)	955°
„ Silver (in reducing atmosphere)						962°
„ Gold	1064°
„ Copper (in air)	1062°
„ Potassium Sulphate	1070°
„ Copper (in reducing atmosphere)						1084°
„ Nickel	1427°
„ Pure Iron	1503°
„ Palladium	1545°
„ Platinum	1750°

Boiling Point at 760 mm. press. of Magnesium			1120°
„	„	„	Antimony 1440°
„	„	„	Lead 1525°
„	„	„	Aluminium 1800°
„	„	„	Manganese 1900°
„	„	„	Silver 1955°
„	„	„	Chromium 2200°
„	„	„	Tin 2270°
„	„	„	Copper 2310°
„	„	„	Iron 2450°

SPECIFIC HEATS AND ELECTRICAL RESISTANCE AT 0°.

ELECTRO-CHEMICAL EQUIVALENTS.

		Specific heat.	Specific resistance.
Aluminium	...	0·22	$0·028 \times 10^{-4}$
Iron	0·11	$0·99 - 0·15 \times 10^{-4}$
Copper	0·093	$0·017 \times 10^{-4}$
Nickel	0·11	$0·08 - 0·11 \times 10^{-4}$
Platinum	...	0·032	$0·108 - 0·11 \times 10^{-4}$
Silver	0·056	$0·016 \times 10^{-4}$
Mercury	...	0·0332	$0·958 \times 10^{-4}$
Glass	0·19	$1·0 \times 10^{15}$
Graphite	...	0·155	$14·3 \times 10^{-4}$
Retort Carbon	...	0·165	$49·0 \times 10^{-4}$

Electrochemical Equivalents.

1 gram equivalent conveys 95640 coulombs (ampère seconds). 1 Ampère Hour therefore produces—

At the cathode.	
1.186	gram. Copper (from cupric salts)
4.0248	„ Silver
1.094	„ Nickel
1.219	„ Zinc
0.0375	„ Hydrogen
At the anode.	
0.2983	„ Oxygen
1.322	„ Chlorine
2.982	„ Bromine
4.730	„ Iodine

DISCHARGE VOLTAGES OF DIFFERENT IONS FROM
AQUEOUS SOLUTION.

On reversing the signs, the values represent the solution tendency.

(a) Cation discharge points.

		volt.		
K.	-2.92	+	0.058	log. C.
Na.	-2.52	+	„	„
Mg.	-1.27	+ $\frac{1}{2}$	„	„
Zn.	-0.48	+ $\frac{1}{2}$	„	„
Fe.	-0.15	+ $\frac{1}{2}$	„	„
Cd.	-0.12	+ $\frac{1}{2}$	„	„
Tl.	-0.04	+	„	„
Co.	-0.01	+ $\frac{1}{2}$	„	„
Ni.	+0.06	+ $\frac{1}{2}$	„	„
Pb.	+0.16	+ $\frac{1}{2}$	„	„
Sn.	+0.18	+ $\frac{1}{2}$	„	„
H.	+0.277	+	„	„
Cu.	+0.62	+ $\frac{1}{2}$	„	„
Ag.	+1.08	+	„	„
Hg.	+1.14	+ $\frac{1}{2}$	„	„
Au.	+1.78	+	„	„

(b) Anion discharge points.

	$S'' - 0.28 + \frac{1}{2} 0.058 \log C.$		
$4OH' (-\rightarrow O_2 + 2H_2O)$	$+ 0.69 +$	"	"
	$I' + 0.82 +$	"	"
	$Br' + 1.36 +$	"	"
	$Cl' + 1.63 +$	"	"
	$F' + 2.18 +$	"	"

C = Ionic Concentration at 25°

Reduction Potentials (normal solutions).

Cu^{\cdot}	$\rightarrow Cu^{\cdot\cdot}$	$+ 0.45$
$Fe(CN)_6^{\cdot\cdot\cdot\cdot}$	$\rightarrow Fe(CN)_6^{\cdot\cdot\cdot}$	$+ 0.68$
$Fe^{\cdot\cdot}$	$\rightarrow Fe^{\cdot\cdot\cdot}$	$+ 0.93$
$Hg_2^{\cdot\cdot}$	$\rightarrow 2Hg^{\cdot\cdot}$	$+ 1.10$
Tl^{\cdot}	$\rightarrow Tl^{\cdot\cdot}$	$+ 1.52$
$Co^{\cdot\cdot}$	$\rightarrow Co^{\cdot\cdot\cdot}$	$+ 2.08$
$Pb^{\cdot\cdot}$	$\rightarrow Pb^{\cdot\cdot\cdot}$	$+ 2.08$

Potentials of Oxidation Reactions.

H_2	$+ 2OH' \rightarrow 2H_2O$	$- 0.54$
$2H_2O$	$\rightarrow O_2$	$+ 4H^{\cdot} + 1.51$
$Cr^{\cdot\cdot\cdot}$	$+ 4H_2O \rightarrow HCrO_4'$	$+ 7H^{\cdot} + 1.58$
$Mn^{\cdot\cdot}$	$+ 2H_2O \rightarrow MnO_2$	$+ 4H^{\cdot} + 1.63$
$Pb^{\cdot\cdot}$	$+ 2H_2O \rightarrow PbO_2$	$+ 4H^{\cdot} + 1.72$
MnO_2	$+ 2H_2O \rightarrow MnO_4'$	$+ 4H^{\cdot} + 1.81$
O_2	$+ H_2O \rightarrow O_3$	$+ 2H^{\cdot} + 1.2$

* The normal calomel electrode = -0.564 (at 25°)
is here taken as the standard.

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